PECULIARITIES OF THE REACTIONS OF AUTOHYDROGENOLYSIS OF

ORGANOSULFUR COMPOUNDS IN THE PRESENCE OF MAICIL

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The reactions of hydrogenolysis of representatives of various classes of organosulfur compounds (hexyl mercaptan, dihexyl sulfide, dihexyl disulfide, thiophene, and concentrates of sulfides isolated from diesel fuel) in the presence of MAICl₄ (M = Li, Na, K) was studied. High degrees of conversion of sulfur-containing compounds in hydrogenolysis reactions are achieved at substantially low temperatures (150-250°C). The reactions of elimination of sulfur from organosulfur compounds with the formation of H₂S occur with the participation of hydride ions, formed in the process; in this case the solvent performs the function of a proton donor. In liquid conversion products the presence of aromatic hydrocarbons is detected. The scheme of occurrence of the coupled reactions occurring in the presence of MAICl₄ is cited.

RESULTS AND DISCUSSION

Two types of reactions of desulfuration of organosulfur compounds with the elimination of H_2S are known. The reactions of the first type [1, 2], proceeding at 250-415°C, pressure 1-10 MPa, and a 50-1000-fold excess of H_2 in the presence of aluminum-cobalt-molybdenum or aluminum-nickel-molybdenum catalysts, are the basis of industrial processes of hydropurification of crude petroleum

 $R-CH_2-SH + H_2 \rightarrow R-CH_3 + H_2S$ $R - CH_3-S-CH_2-R + 2H_2 \rightarrow 2R-CH_3 + H_2S$

The reactions of the second type - catalytic desulfuration of sulfur-containing hydrocarbons without the introduction of exogenous hydrogen in the presence of α -Fe, oxides of aluminum and zinc, aluminosilicate, kaolin, platinum on charcoal, and certain other catalysts [1, 3] - proceed at 200-600°C and a pressure of 1-5 MPa, and are of increased interest thanks to their simplicity and many technological advantages. And yet, in the presence of these catalysts hydrogenolysis proceeds with low degrees of conversion, and the reaction mechanism has not been established.

Complex compounds MAlCl₄ (M = Li, Na, K) are promising catalysts for the process without H_2 .

Under mild conditions (150-250°C, atmospheric pressure), the decomposition of organosulfur compounds (Tables 1, 2) is accompanied by a high yield of H_2S and the formation of gaseous and liquid hydrocarbons of various structure and composition (Tables 3, 4). The gaseous products contain not only saturated and olefinic C_2-C_4 hydrocarbons but also H_2 (Table 4), while the liquid products contain aromatic hydrocarbons [toluene, benzene, ethylbenzene, xylene, etc. (Table 5)].

The degree of desulfuration of organosulfur compounds in the presence of MAlCl₄ depends on the nature of the solvent (Fig. 1). In the presence of aliphatic hydrocarbons (dodecane, the naphthene-paraffin fraction of hydrocarbons), the desulfuration reaction proceeds to a substantially more profound degree than in arenes (the aromatic fraction of hydrocarbons, 200-300°C) - this agrees with the known facts [2], that the energy of stripping of a hydrogen atom from mono- and bicyclic aromatic hydrocarbons is rather high.

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		[S], % by	weight	Molecular
Organosulfur compound	Bp, °C (10 mm Hg)	total	func- tional	weight
Hexyl mercaptan Dihexyl disulfide Dihexyl sulfide Thiophene Concentrate I	150 230 159–161 84,2 240–250	27,1 15,8 27,4 38,1 16,4	27,1 15,7 27,1 13,6	118 202 234 84 192
Concentrate II	270-280	14.4	12.3	208

TABLE 1. Characteristics of Organosulfur Compounds

TABLE 2. Chemical Composition (% by weight) of Sulfide Concentrates [10]

		Cor	mposition of	raw materi	ial*	
Concentrate*	1	2	. 3	4	5	6
I II	3 0 20	44 20	11 15	Traces 20-25	2 3	2 3
$ \frac{1}{1} 1$	5) () s	-R; 2) [; 6) R-S-	, () R.	(); 3)	, () s	;

TABLE 3. Distribution of Sulfur in the Hydrogenolysis Products⁺

· · · · ·	Sulfur content (calculated per 100 g of raw material), g					
Organosulfur compound	initial solution	liquid products	gaseous products	on catalyst		
Hexyl mercaptan Dihexyl disulfide Dihexyl sulfide Thiophene Concentrate I Concentrate II	1,00 1,00 1,00 1,00 1,00 1,00	0,13 0,40 0,50 0,85 0,44 0,24	0,84 0,57 0,46 0,14 0,52 0.75	0,03 0,03 0,04 0,01 0,04 0,04 0,01		

⁺(NaAlCl₄; 250°C; 60 min; solvent - dodecane.

Noteworthy is the comparatively high content of H_2S in the products of hydrogenolysis of thiophene (Table 4), which is explained by a decrease in the contribution of reactions of cracking of hydrocarbons in this case and, as a result, by a decrease in the amount of gas liberated.

The determining influence of the donor of hydride ions in the system on the degree of hydrogenolysis of sulfur-containing compounds is confirmed by a comparison of the results of hydrogenolysis of sulfide concentrates of two types, differing in structuro-group composition (Table 2). Concentrate I contains primarily mono- and bithiacyclanes, while in concentrate II the proportion of concentrated four-ring thiacyclanes is significantly higher. It is known that polycyclic condensed cycloalkanes are aromatized to a greater degree than mono-cyclic cycloalkanes [4]. The amount of hydrogen formed in the system is correlated with the yield of arenes [4]. Thus, in concentrate II the amount of H_2 formed is higher than in concentrate I under the same conditions of the hydrogenolysis reaction (Table 4). This is correlated with data on the residual sulfur content in concentrates I and II (Table 3).

It is important to note that the active form of hydrogen in its reactions with the elimination of sulfur and hydrogenation of olefins is hydride ions, whereas molecular hydrogen introduced into the reaction zone has no effect on these processes (Table 4). The aggregate of experimental facts permits us to assert that the proton donors in the hydrogenolysis of

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	Amount of				Ü	ompositi	on of gas	eous pro	ducts, %	by weight			
Compound	gas lib- erated, % by weight	H ₂	CH	C ₂ H,	C ₂ 116	H_2S	C ₃ H ₆	C ₃ II ₆	i-C ₄ H ₁₀	i-, n-C,H 	n-C4H ₁₀	trans- C ₄ H ₈	cis- C4H ₈
Hexyl mercaptan	2,90	0,05	0'0	2,14	0,76	12,76	Traces	14,18	37,48	9,68	22,86	I	1
Hexyl mercaptan [*]	2,88	I	0,07	2,10	0,78	12,77	Traces	14,13	37,50	9,70	22,95	I	1
Dihexyl disulfide	1,60	0,06	0,07	1,92	2,26	16,66	1	15,58	45,73	Traces	17,72	1	1
Dihexyl sulfide	1,30	0,06	0,11	2,27	1,15	16,49	Traces	12,20	46,13	Traces	21,59	I	1
Thiophene	0,11	0,26	4,06	3,31	1,58	34,87	0,84	1,42	30,45	0,34	22,87	1	. I .
Concentrate I	2,60	0'0	3,78	8,85	2,87	9,84	0,33	10,74	24,73	21,85	13,70	3,20	0,05
Concentrate II	1,85	0,17	3,88	9,23	3,86	21,26	0,21	11,42	22,79	10,43	16,75	1	1
Aromatic fraction 200-300°C	0,10	0'0	0 , 06	2,51	0,03	1	1	13,96	13,11	43,51	20,14	3,25	3,42
Naphtheno-paraffin frac- tion of diesel fuel	3,56	0,62	0,04	1,12	4,51]	0,31	23,97	38,26	5,67	24.83	0,57	0,10
Dodecane	3,21	0,54	0,05	1,57	4,11	1	0,28	21,19	44,68	4,21	22,19	1,04	0,14

 $\overset{\rm X}{\rm The}$ experiment was conducted with delivery of ${\rm H}_2$ to the reaction zone.

Hydrogenol- ysis prod- ucts	Hexyl mer- captan in dodec- ane	Thio- phene in dodecane	Dode- cane	Hydrogenolysis products	Hexyl mercaptan in dodec- ane	Thioph- ene in dodecane	Do- decane
Hexane Hexene Isooctane Octene	0,06 0,33 - -	0,12 0,21 0,66 0,35	0,52 0,24 	Toluene Xylenes Unidentified aromatic	3,42 6,95 3,94	0,74 1,30 5,29	0,82 1,56 3,78
Benzene Ethylbenzene	0,30 0,60	0,09	0,25 0,08	Isododecane Dodecane	2,27 82,13	4,66 86,58	3,15 89.60

TABLE 5. Composition (% by weight) of Liquid Hydrogenolysis Products (NaAlCl₄, 250°C)



Fig. 1. Dependence of the degree of hydrogenolysis of hexyl mercaptan (1, 5), dihexyl disulfide (2, 6), dihexyl sulfide (3, 7), and thiophene (4, 8) on the time of exposure using the solvents: 1-4) naphthenoparaffin fraction of diesel fuel; 5-8) aromatic fraction 200-300°C.

organosulfur compounds in the presence of $MAlCl_4$ are the aliphatic hydrocarbons used as the solvents; reactions of this type proceed in the presence of electrophilic catalysts with reduced acidity in comparison with $AlCl_3$, with the participation of linear and/or branched aliphatic hydrocarbons as proton donors.

The presence of organosulfur compounds in the products of the decomposition reaction, like that of aliphatic hydrocarbons (Table 4) and molecular hydrogen in appreciable amounts in the case of hydrogenolysis in the presence of $MAlCl_4$, is an indication that in addition to the ability to conduct the reaction with quantitative elimination of H_2S from sulfur-containing hydrocarbons and the ability for destruction of hydrocarbons (from the light petroleum fractions, fuel oils, and asphalts to polymers) [5], the $MAlCl_4$ are at the same time catalysts of dehydrogenation. Since, according to [6], $MAlCl_4$ are active in the form of the aqua-complex H^+ [NaAlCl₄OH]⁻, then evidently

$$\sim CH_2 - CH_2 - CH_3 + H^+[NaAlCl_4OH]^- \rightarrow \sim CH_2 - CH_2 - CH_3[NaAlCl_4OH]^- + H^+H^- \rightarrow \sim CH = CH - CH_3 + H_2 + H^+[NaAlCl_4OH]^-$$

The consumption of hydrogen for the formation of H_2S with the participation of aliphatic hydrocarbons as proton donors leads not to an increase in the proportion of unsaturated compounds in the liquid reaction products (Fig. 2) but to the formation of aromatic hydrocarbons (Table 5). The IR and UV spectra of the reaction products do not contain characteristic bands corresponding to C=C, but absorption bands 1500-1480 cm⁻¹ and 265-260 nm, respectively, corresponding to the vibrations of the ring in aromatic hydrocarbons, appear. This is an indication that MAICl₄ are catalysts of the aromatization of aliphatic hydrocarbons, participating in reactions of redistribution of hydrogen [7]. Analogous results were also obtained in the catalytic destruction of hydrocarbons, in particular, dodecane (Table 5), which directly confirms the activity of the catalyst MAICl₄ in reactions of dehydrocyclization of linear hydrocarbons.



Fig. 2. Change in the iodine number in conversion products of dodecane under the action of NaAlCl₄: 1) 200; 2) 250°C.



Fig. 3. Hydrogen content in gaseous hydrogenolysis products of hexyl mercaptan in the presence of $LiAlCl_4$ (1-3), $NaAlCl_4$ (4-6), $KAlCl_4$ (7-9) at 180 (1, 4, 7), 225 (2, 5, 8), and 250°C (3, 6, 9).

It is characteristic that the kinetic curves showing a change in the H_2 content in the conversion products pass through a maximum (Fig. 3). This is evidently due to the fact that at the first stage the rate of the dehydrogenation of hydrocarbons of the solvent is higher than the rate of formation of H_2S , and at later stages the reactions of binding of the sulfur being eliminated and the reaction of hydrogenation of light olefins are intensified with a simultaneous decrease in the rate of formation of hydrogen.

EXPERIMENTAL

Calcined (200°C) LiCl, NaCl, and KCl, as well as AlCl₃ purified by the method of sublimation, were used in the synthesis of the catalysts. The catalyst was prepared by sintering stoichiometric amounts of MCl and AlCl₃ at 180°C according to [8]. The hydrogenolysis reaction was conducted in a glass reactor (100 cm³) above a melt of the catalyst at a ratio of the catalyst to the solution of the sulfur-containing compound equal to 1/4 (by weight) in nitrogen medium. For the experiments we used solutions of organosulfur compounds with a total content of 1.0% by weight S; the naphtheno-paraffin fraction of diesel fuel, the aromatic fraction 200-300°C, or dodecane was used as the solvent.

The analysis of the gaseous and liquid reaction products was performed chromatographically (chromatographs for the analysis of gases: LKhM-8, MD-6; 6% liquid petrolatum, applied to tripolite of the Zikeevsk quarry, column length 3 m; for the analysis of liquids: Tsvet-100, SE-30, temperature of evaporator 200°C). The total sulfur content in the products was determined by the method of combustion, and the content of functional sulfur by the method of potentiometric titration [9]. The UV and IR spectra of the liquid products were recorded on a UR-20 instrument in the region of 800-200 nm and 4000-400 cm⁻¹, respectively. The content of unsaturated hydrocarbons in the initial raw material and in the reaction products was monitored according to the iodine numbers. The objects of study were representatives of various classes of organosulfur compounds: hexyl mercaptan, dihexyl sulfide, dihexyl disulfide, and thiophene. Hydrogenolysis of polycyclic heteroatomic compounds was studied on sulfide concentrated isolated from diesel fuel of Arlansk petroleum (Table 1). Sulfide concentrates I and II contained 97.5 and 94.0% by weight organosulfur compounds, including $\geq 80\%$ sulfides. Thiophene compounds in these concentrates accounted for 16.5 and 14.0% by weight, respectively. The sulfide portion of the concentrate is presented in Table 2.

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