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Chemical transformations of organic sulfides during hydrogenolysis in the presence of metal chloride complexes

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Desulfurization of organic sulfides in hydrocarbon solvents in the presence of aqua complexes of metal chlorides $H[MAlCl_4OH]$ that exhibit lower acidity as compared to $AlCl_3$ proceeds under mild conditions (450—525 K, atmospheric pressure) without external introduction of hydrogen. The process occurs with cleavage of C—S bonds and through intermediate formation of mercaptans to give H_2S and the corresponding hydrocarbons. The reaction is accompanied by cleavage of C—C bonds in the groups surrounding the organosulfur moiety, in thiacyclane rings, as well as in hydrocarbon solvent molecules, resulting in the formation of a wide spectrum of gaseous and liquid products.

Key words: organosulfur compounds, sulfides, desulfurization, hydrogenolysis, catalyst.

Catalytic processes that proceed without external introduction of molecular hydrogen into the reaction zone at relatively low temperatures (450—525 K) and atmospheric pressure attract special attention among reactions of desulfurization of organosulfur compounds. $AlCl_3$, $GaCl_3$, $TiCl_4$, $SnCl_4$, $HgCl_2$, $PdCl_2$, $PtCl_2$, and $TlCl_3$[1—6] were described as catalysts. In particular, $AlCl_3$ causes decomposition of di-*tert*-octylsulfide to afford diisobutylene and *tert*-octylmercaptan. Aluminum halides catalyze transformations of α-methylthiophane, thiacyclohexane, *etc.* In the presence of $AlCl_3$, alkylation of benzene with di-*tert*-butyl- and isopropylphenylsulfides is also possible.[5] According to relative activity in degrading the C—S bond, metal halides are arranged in the series $AlBr_3 > AlCl_3 > TiCl_4 > SnCl_4 > GeCl_4$, which agrees with the series of electron-withdrawing activity of these compounds. However, the relatively high acidity of metal halides, especially $AlBr_3$, $AlCl_3$, $SnCl_4$, *etc.*, determines their high activity not only as catalysts of desulfurization of organosulfur compounds by hydrogenolysis but also as catalysts of secondary processes, such as polymerization, aromatization of hydrocarbons, degradation, and linking of molecules, resulting, in some cases, in insufficient selectivity of these catalysts. In addition, the chemical natures of active centers, as well as the ways of transformation of organosulfur compounds, are not clear in many cases.

Therefore, it seemed worthwhile to study aqua complexes of $AlCl_3$ with alkali metal chlorides[2,7,8] in the form of Brönsted acids $H[MAlCl_4OH]$ that are characterized by reduced acidity as compared with $AlCl_3$,[9] as catalysts of desulfurization of organosulfur compounds for an example of hydrogenolysis of organic sulfides. As a consequence of the above properties of these complexes, the catalyst has higher selectivity and maintains sufficiently high activity.

Table 1. Composition of gaseous products of hydrogenolysis of individual organosulfur compounds in dodecane

Compound	Amount of liberated gas (mass %)	Composition of gaseous products (mass%)							
		H_2S	H_2	CH_4	ΣC_2	ΣC_3	*i*-C_4H_{10}	*i*- and *n*-C_4H_8	*n*-C_4H_{10}
Hexylmercaptan	2.90	12.76	0.05	0.09	2.90	14.18	37.48	9.68	22.86
Hexylmercaptan*	2.88	12.77	—	0.07	2.88	14.13	37.50	9.70	22.95
Dihexyldisulfide	1.60	16.66	1.60	0.07	4.18	15.58	45.73	Traces	17.72
Dihexylsulfide	1.30	16.49	0.06	0.11	3.42	12.20	46.13	Traces	21.59
Thiophene	0.11	34.87	0.26	4.06	4.89	2.26	30.45	0.34	22.87
Dodecane**	3.21	—	0.54	0.05	5.68	21.47	44.68	4.21	22.19

Note. Reaction conditions: 423 K, $H[MAlCl_4OH]$ (1 mol L^{-1}), 0.5 h. * Experiment was carried out with feeding of H_2 into the reaction zone. ** The yield of *t*-C_4H_8 was 1.04 and that of *cis*-C_4H_8 was 0.14 mass %.

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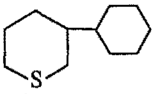
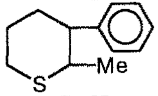
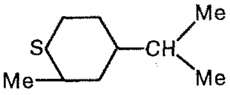
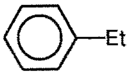
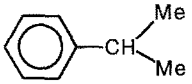
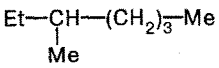
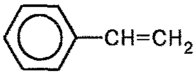
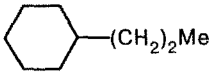
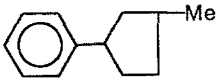
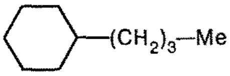
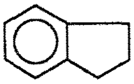
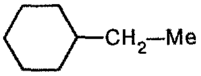
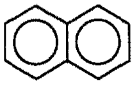
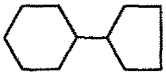
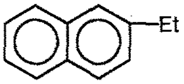
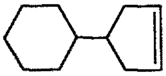
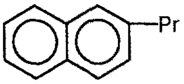
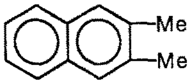
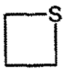
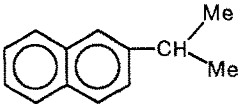
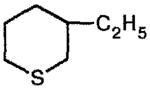
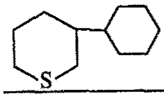
Table 2. Composition of gaseous products of transformation of some cyclic sulfides

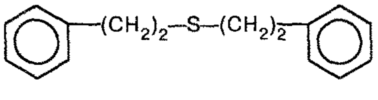
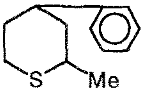
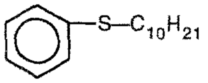
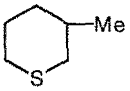
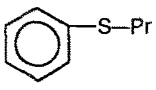
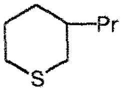
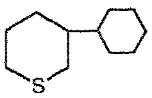
Products of 3-cyclohexyl-thiacyclohexane transformation	Composition (mass %)	Reaction time /min	Products of 2-methyl-4-phenylthiacyclohexane transformation	Composition (mass %)	Reaction time /min
	15	60		15	60
n-C_9H_{20}	3.5	1.0	n-$C_{12}H_{26}$	30.3	26.9
n-$C_{10}H_{22}$	10.2	2.7	i-$C_{12}H_{26}$	34.0	36.8
n-$C_{11}H_{24}$	10.8	0.8		7.1	—
n-$C_{11}H_{26}$	29.9	32.6		—	3.4
i-$C_{12}H_{26}$	12.5	22.3		2.2	3.9
 $\mathrm{Et{-}\underset{\displaystyle Me}{\underset{\vert}{C}}H{-}(CH_2)_3{-}Me}$	2.8	4.7		5.0	1.9
	11.3	11.9		4.9	5.2
	2.5	1.7		6.9	4.7
	1.5	2.0		1.6	—
	8.7	16.2		3.8	6.5
	—	2.8		1.3	2.4
	1.8	—		2.9	4.6
	1.3	—		—	3.7
	0.9	—	—	—	—
	2.3	1.3	—	—	—

Note. Reaction conditions: 523 K, $H[NaAlCl_4OH]$, dodecane.

Catalytic systems of $H[MAlCl_4OH]$ type allow one to carry out hydrogenolysis of different classes of organosulfur compounds, sulfides, disulfides, mercaptans, *etc.*,[10–16] under mild experimental conditions (450—525 K, atmospheric pressure) and without using molecular hydrogen. In this case, not only a catalyst in the form of Brönsted acid, but also a hydrocarbon solvent, serve as a proton donor.[11]

Desulfurization of organosulfur compounds is in all cases accompanied by the formation of gaseous and

Table 3. Rate constants of desulfurization of some sulfides

Acyclic sulfides	Rate constant, $k\cdot 10^4/\mathrm{s}^{-1}$	Cyclic sulfides	Rate constant, $k\cdot 10^4/\mathrm{s}^{-1}$
	8.5		6.7
	7.8		4.5
	5.5		3.3
i-C_5H_{11}—S—n-Pr	3.3		2.5
t-C_6H_{13}—S—n-C_6H_{13}	2.3		2.0
n-C_6H_{13}—S—n-C_6H_{13}	1.8		0.3

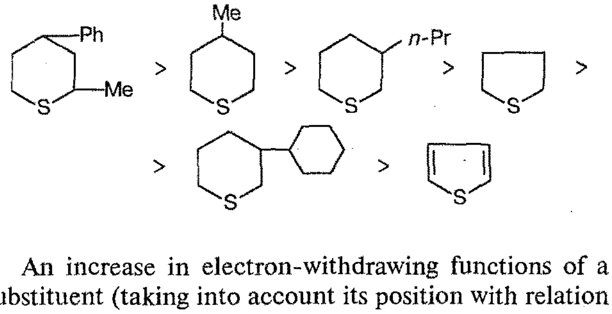
Note. Reaction conditions: 533 K, H[NaAlCl$_4$OH], dodecane.

liquid products. The composition of gaseous products is uniform (H_2S, H_2, C_1—C_5 hydrocarbons), and the amount of H_2S in a gas may reach 40 mass % (Table 1). As can be seen from the example of desulfurization of sulfides (Table 2), the composition of liquid products depends on the chemical structure of the organosulfur compound.

The reactivity of organosulfur compounds changes in the following order: mercaptans > disulfides > sulfides > thiophene. In a series of compounds belonging to one class (using the example of hydrogenolysis of organic sulfides, Table 3), the reactivity changes as follows:

a) acyclic sulfides: Ph—$(CH_2)_2$—S—$(CH_2)_2$—Ph > Ph—S—$C_{10}H_{21}$ > Ph—S—Pr > i-C_5H_{11}—S—H—Pr > t-C_6H_{13}—S—H—C_6H_{13} > n-C_6H_{13}—S—C_6H_{13};

b) cyclic sulfides:



An increase in electron-withdrawing functions of a substituent (taking into account its position with relation to the sulfur atom in thiacyclane nucleus) favors the weakening of the C—S bond. A degree of branching of hydrocarbon moiety benefits the proceeding of desulfurization of organic sulfides, that also results from an increase in the electron-withdrawing functions of a substituent. The reactivity of organic sulfides decreases in the presence of bulky substituents which are capable of creating steric hindrances during hydrogenolysis.

The composition of gaseous and liquid products of desulfurization of organosulfur compounds (see Tables 1 and 2) suggests a single mechanism of their transformation associated with the hydrolysis of C—S bond and formation of H_2S (probably, through the corresponding mercaptans), as well as with heterolytic break of C—C bonds in thiacyclane nuclei and surrounding hydrocarbon fragments. A hydrocarbon solvent participates in the complex chemical process as a proton donor and reagent (heterolytic cleavage of C—C bonds takes place). In particular, we found among the products of transformation of dodecane catalyzed with H[NaAlCl$_4$OH] (573 K, 1 h)[11] (mass %): hexane — 0.52; hexene — 0.24; benzene — 0.25; ethylbenzene — 0.08; toluene — 0.82; xylene — 1.56; i-$C_{12}H_{26}$ — 3.15; dodecane — 89.60; unidentified products — 3.78.

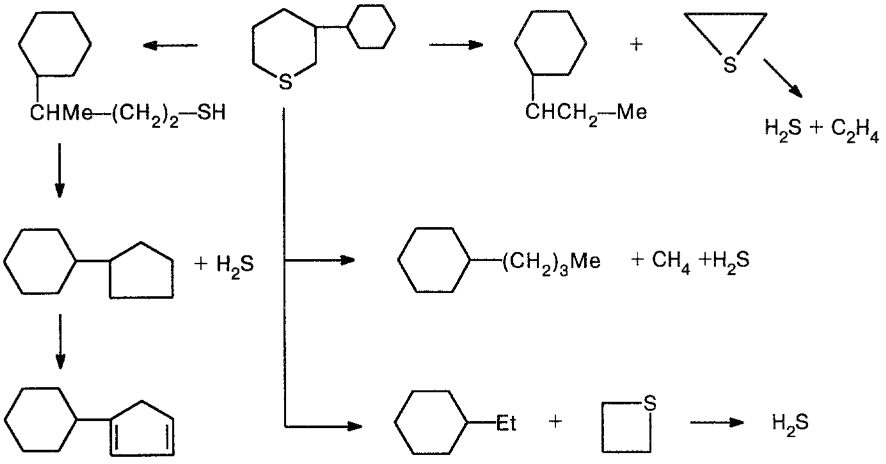
From the hydrogenolysis of 3-cyclohexylthiacyclo hexane and 2-methyl-4-phenylthiacyclohexane in the presence of H[NaAlCl$_4$OH] (see Table 2) it follows that the process proceeds as a combination of parallel-sequential electrophilic reactions:

a) hydrogenolysis of 3-cyclohexylthiacyclohexane in dodecane (Scheme 1).

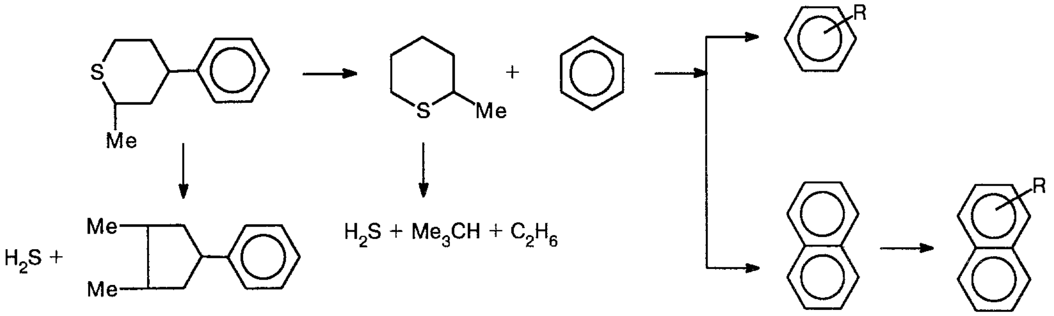
b) hydrogenolysis of 2-methyl-4-phenylthiacyclohexane in dodecane (Scheme 2).

The absence of mercaptans among the liquid products even at early stages (5—10 min) of the process after

Scheme 1



Scheme 2



exposition of both thiacyclanes (523 K) for 0.5—1 h engages our attention. Nevertheless, during pure thermal decomposition and also in the presence of oxide catalysts (*e.g.*, alumocobaltmolybdenum catalysts) with the participation of molecular hydrogen, hydrogenolysis of thiacyclanes proceeds through the step of formation of mercaptans.[17] Taking into account these experimental data and the fact that the rate of mercaptan hydrogenolysis is one to two orders of magnitude higher than that of thiocyclanes, one may assume that mercaptans, like thiirane, thiacyclopropane, 2-ethylcyclohexane, and dimethylthiacyclohexane (see Table 2), participate in the process as intermediates. Saturated aliphatic hydrocarbons (C_8—C_{11}, i-$C_{12}H_{26}$, *etc.*) are formed as a result of electrophilic transformations of a hydrocarbon solvent (dodecane) and may then afford olefins, naphthenes, and arenes.

Experimental

Analysis of gaseous reaction products was carried out chromatographically (LKhM-8, MD-6, 6 % of Vaseline oil supported on tripoli from a Zikeev mine, length of column 3 m). For the analysis of liquid reaction products we jointly used a KRATOS mass spectrometer and a CARLO-ERBA Strumentazione chromatograph. Heating was carried out in a programmed regime from 323 to 473 K, the rate of heating was 20 deg min^{-1}, and the temperature of the probe and separator was 523 K. The flow separator was of an open type; the sample amount was 0.2—025 μL. A quartz column, 26 m in length, was used, the internal diameter was 0.3 mm, the phase was SE-5, and the rate of helium flow was 5 mL min^{-1}. The fractions obtained by chromatographic separation were automatically injected into the ion source. Mass spectra were recorded within the 16—600 mass region. The energy of the ionizing electrons was 18, 20, 22, 24, and 70 eV, the accelerating voltage was 3.5 kV, the cathodic filament current was 3.0 A, and the temperature in the source of positive ions was 523 K.

The total sulfur content in the products was determined by a burning method.[20]

For the synthesis of catalysts, calcinated (200 °C) LiCl, NaCl, and KCl and $AlCl_3$ purified by sublimation were used. The catalysts were prepared by caking stoichiometric amounts of MCl and $AlCl_3$ in air at 180 °C according to the previously described procedure.[17] The stability of catalysts and existence of the adsorbed water on the surface of a catalyst were studied on a MOM derivatograph of Paulic—Paulic—Erdey system in inert atmosphere (argon) within the temperature interval 298—273 K, the rate of heating was 5 deg min^{-1}. The activating influence of water (cocatalyst) on electrophilic processes in the presence of $MAlCl_4 \cdot H_2O$ was confirmed[18] with quantum chemical calculations (method of MO LCAO in PPDP/2 approximation) with optimization of equilibrium geometry using the random search method[19] with the accuracy 0.01 Å for bond lengths and 1 deg for valence angles. Data from calculations allowed us to consider the influence of H_2O on the activity of complexes as the result of dissociative adsorption of H_2O on a catalyst surface. Therefore, the structure of electrophilic active centers may be presented as $H^{\delta+}[MAlCl_4OH]^{\delta-}$.

Hydrogenolysis reactions were carried out in a glass reactor (100 cm^3) over melted catalysts in nitrogen with the ratio catalyst : solution of sulfur-containing compound = 1 : 4 (mass %). Solutions of sulfur-containing compounds with a total sulfur content of 1 mass % were used for the experiments; dodecane was used as the solvent.

The following kinetic equation (similar to the Avrami—Erofeev equation)[21] was used for determination of the rate constants of hydrogenolysis of the sulfur-containing compounds:

$$C_\tau = C_{\tau 0}\exp[(-k_{\mathrm{eff}}\tau)^n],$$

where $C_{\tau 0}$ and C_τ are the initial and current concentrations of a compound, respectively, k_{eff} is the effective constant, and n is the reaction order.

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