charged telogen. Lactone (VI) was isolated from the reaction mixture by preparative GLC. The adduct was not isolated as such, since under the preparative GLC conditions it converts into a lactone.

CONCLUSIONS

1. Radical telomerization of trimethylvinylsilane is similar to an analogous reaction of propylene, due to the similar influence of the Me_3Si and CH_3 groups on the neighboring radical center in the growing radical.

2. The telomerization of trimethylvinylsilane with methyl isobutyrate leads not only to the telomers with a normal structure, but also to the formation of an unsaturated compound $Me_3SiCH_2CH{=}CHCH_2CMe_2CO_2Me$.

3. In contrast to Fe(CO), decacarbonyldimanganese effectively initiates the addition of methyl bromoacetate to trimethylvinylsilane.

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A STUDY OF THE PRODUCTS FROM THE HETEROGENEOUS CATALYTIC OXIDATION OF MERCAPTAN

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When processing a mixture of hydrocarbons and organic sulfur compounds in the presence of oxygen a large number of various types of oxygen-containing sulfur compounds are formed as well as H_2S, SO_2, CO, and CO_2 [1, 2].

The problems of studying the mechanism of the catalytic conversion of sulfur compounds involve that of reliable identification of the reaction products which cannot be resolved without using modern physical and chemical methods of investigation.

In this investigation we have studied the products from the heterogeneous catalytic oxidation of ethyl mercaptan by NMR, GC, IR, and mass spectrometry.

EXPERIMENTAL

Ethyl mercaptan was passed over a mixed oxide catalyst at 200°C and a space velocity of 2000 h^{-1} in a mixture with methane and air. The reaction products formed were collected

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TABLE 1. GC Analysis of Products from the Heterogeneous Catalytic Oxidation of Ethyl Mercaptan on Columns with Different Polarity

DNP		SE-30			Assignment	bp, °C
T, °C						
80	110	60	80	110		
2'03"	0'57"	0'47"	0'28"	0'13"	EtSEt	92
13'10"	4'37"	4'20"	1'54"	0'48"	EtSSEt	154
47'40"	20'05"	19'00"	7'05"	2'30"	EtSSSEt	204
—	—	—	—	9'10"	EtSSSSEt	251

in two cold traps arranged in sequence (0 and −78°C). GC analysis was carried out over the temperature range 60-110°C on Tsvet-102 and Tsvet-152 chromatographs, having a thermal conductivity detector and a flame ionization detector, on two glass columns (150 × 0.3 cm) containing 20% dinonyl phthalate (DNP) on Celite 545 and on Chromosorb AW-HMDS with 5% SE-30 silicone, fraction 0.200-0.360 mm. The carrier gas was helium.

The PMR spectra of the reaction products were obtained on a Bruker WM-250 spectrometer with a frequency of 250 MHz at the working temperature of 20°C, and operating in the pulsed regime. The chemical shift (CS) is presented in parts per million (ppm) of the internal standard of TMS. Deuterochloroform was used as the solvent. The IR spectrum of the products from mercaptan oxidation was recorded on a UR-20 spectrophotometer in the region 400-3700 cm^{-1} in a nondiscriminating cuvette having a layer thickness of 0.05 mm and KBr windows, without using a solvent. The mass spectrum was obtained on a Varian MAT-111 chromatograph-mass spectrometer. The electron ionization energy was 50 eV. The gas chromatography column (150 × 0.31 cm) contained 5% SE-30 silicone on N-AW-DMCS Chromaton.

DISCUSSION

GC analysis of the oxidation products revealed four substances in the ratio 1:80:15:1, the retention times (t_R) of which on the column containing DNP and SE-30 at various temperatures are presented in Table 1. The retention times of the first two products corresponds completely to the retention times of standard diethyl sulfide and diethyl disulfide under identical GC analysis conditions.

If the oxidation of ethyl mercaptan takes place by the pathway of an increase in the S—S chain then the other two products may be diethyl trisulfide and diethyl tetrasulfide. To identify all four products graphs were constructed for the dependence of the logarithm of the retention time ($\log t_R$) on the boiling point T_{bp} (Fig. 1) and the number of sulfur atoms in the postulated diethyl polysulfides (Fig. 2). The boiling point data for diethyl trisulfide and diethyl tetrasulfide [3] are 204 and 251°C respectively.

To confirm the proposed assignment and to prove that the compounds obtained do not contain groups containing sulfur—oxygen a chromatographic-mass spectrometric analysis was conducted of the oxidation products. The presence of ions with mass numbers 122, 154, and 186 in the mass spectrum of the molecular ions indicates the presence of Et_2S_2, Et_2S_3, and Et_2S_4 in the reaction products. Data on the fragmentation of these compounds are in good agreement with the proposed structure of the compounds formed (see Table 2).

The composition of the fragmentation products from diemthyl trisulfide [4] corresponds on the whole to the composition of the fragmentation products from the substances identified, as presented in Table 2.

The PMR spectrum of the oxidation products shows that bridging methylene groups bound with the sulfur atom are absent in the reaction products. They should be in the region of 1.7-1.9 ppm [5], where there is no signal on the spectrogram. A signal is also not observed from methyl and methylene radicals bound with oxygen. In the region 2.7-3.0 ppm quartets are clearly expressed from the four methylene groups present in the ethylene substituents (2.70; 2.89; 2.97; 2.99 ppm), which belong to sulfide compounds having a different number of sulfur atoms. Similarly, in the region 1.32-1.44 ppm triplets are observed from the methyl groups present in ethyl, which belong to sulfide compounds having a different

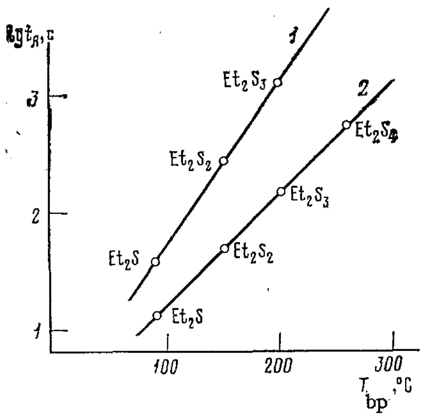

Fig. 1

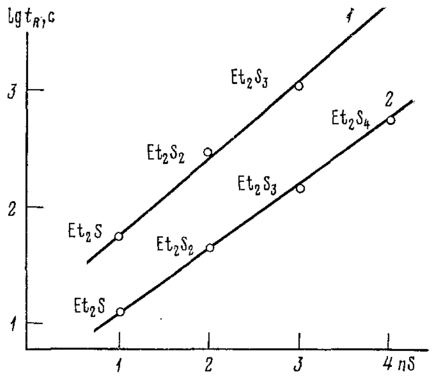

Fig. 2

Fig. 1. Dependence of the logarithm of the retention time (t_R) on the boiling points of the diethyl sulfides. 1) DNP; 2) SE-30; separation temperature 110°C.

Fig. 2. Dependence of the logarithm of the retention time (t_R) on the number of sulfur atoms in the diethyl sulfides. 1) DNP; 2) SB-30; separation temperature 110°C.

TABLE 2. Chromatographic-Mass Spectrometric Analysis of Products from the Oxidation of Ethyl Mercaptan

m/z	Fragment identified	Peak intensity of fragments, %		
		Et_2S_2	Et_2S_3	Et_2S_4
44	CS	38	81	61
45	HCS	27	80	95
46	CH_2S	11	87	42
47	MeS	23	34	33
61	EtS	18	100	100
62	EtSH	13	55	56
64	SS	18	41	42
66	HSSH	100	41	61
93	EtSS	–	26	63
94	EtSSH	80	28	64
122	EtSSEt	98	–	12
154	EtSSSEt	–	59	33
186	EtSSSSEt	–	–	15

number of sulfur atoms. The ethyl quartets having a CS of 2.70 and 2.89 ppm were identified by means of standard samples of diethyl sulfide and diethyl disulfide.

In the IR spectrum of the mercaptan oxdiation products absorption bands were observed in the regions of 500, 600, 950-1000, 1250-1450, and 2800-3000 cm^{-1}. the band at 450 cm^{-1} characterizes the S—S bond, that at 695 cm^{-1} characterizes the EtS group. The bands in the regions 1300-1450 and 2800-3000 $cm^{-1}$are assigned to the deformation and stretching vibrations of the CH_3 and CH_2 groups in C_2H_5 [6, 7]. The absence of intense absorption bands at 1100-1150 cm^{-1} indicates that the S—O bond is not formed in the reaction products, while the absence of a band at 1325 cm^{-1} indicates the absence of the SMe group [6, 7].

A comparison of the spectrum of one of the oxidation products to which peak 2 corresponds on the chromatogram, with the spectrum of EtSSEt shows them to be completely identical; a certain increase in the intensity of the band at 480 cm^{-1} indicates a small impurity of a compound containing the SSS or the SSSS group.

Based on the data in Table 3, we may conclude that EtSEt, EtSSEt, EtSSSEt, and EtSSSSEt are formed in the heterogeneous catalytic oxidation of ethyl mercaptan.

Thus, in contrast to the data known in the literature on the formation of various classes of substances incorporating sulfur—oxygen-containing groups in the oxidation of sulfur-containing compounds, the oxidation of ethyl mercaptan over oxide catalysts takes

TABLE 3. Summary Table of the Results from Analyzing the Products from the Heterogeneous Catalytic Oxidation of Mercaptan over a Mixed Oxide Catalyst

GC analysis	Retention time corresponds to the mono-, di-, tri-, and tetrasulfides The boiling points correspond to the mono-, di-, tri-, and tetrasulfides.
Chromatograph-mass spectrum	The molecular ion fragments correspond to the molecular weight of the mon-, di-, tri-, and tetrasulfides. Other substances not detected.
PMR spectrum	Four types of ethyl have been detected in compounds with a different number of sulfur atoms. Bridging methylene bound with the sulfur atom is absent; radicals bound with an oxygen atom are absent.
IR spectrum	Absorption bands corresponding to the S–S, C_2H_5–S, CH_3, and CH_2 bonds are present. Oxygen–sulfur and methyl–sulfur bonds are absent.

place selectively to a greater degree, to give only polysulfides. The difference in boiling points readily enables them to be separated and the individual components to be used in preparative organic synthesis (such as, for example, the predominantly formed diethyl disulfide) or as a source of free radicals in vulcanizing. It is known [8] that polysulfides may serve as effective chain transfer agents in radical polymerization reactions. The results obtained are of considerable interest from the viewpoint of: a) obtaining sulfur-containing compounds in a single class (aliphatic polysulfides); b) ease of separating liquid sulfur-containing products after removing them from natural gas; c) the absence of catalyst deactivation, in contrast to the use, for example, of zinc oxide, which forms ZnS, which is only poorly amenable to regeneration.

CONCLUSIONS

Compounds of one class are formed in the heterogeneous catalytic oxidation of ethyl mercaptan, viz. aliphatic polysulfides. Diethyl di-, tri-, and tetrasulfides have been identified by gas chromatography, infrared spectroscopy, and proton magnetic resonance.

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