INORGANIC AND ANALYTICAL CHEMISTRY

ANALYSIS OF THE REACTION PRODUCTS OF HYDROGEN SULFIDE WITH ETHYLENE AND PROPYLENE OXIDES

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UDC 543.8:546.221+547.422.22-31

The basic products of the reaction of hydrogen sulfide with olefin oxides are β-hydroxyalkyl mercaptans and bis-(β-hydroxyalkyl)-sulfides, which, as is well known, are used as starting materials for the production of polymers, lubricating oils, dyes, plasticizers, biologically active substances, etc. In connection with the wide use of the compounds studied, the development of methods of their analysis is of practical and theoretical interest. The determination of the substances by volumetric methods is well known [1]. However, in a number of cases, especially in the analysis of mixtures of products, volumetric methods cannot be successfully used without preliminary separation of the components. In recent years, many methods of identification and quantitative determination of compounds without their preliminary isolation in pure form have been created on the basis of thin-layer chromatography (TLC). An advantage of this method is the high sensitivity, permitting the detection of a very small quantity of the substance (down to 0.05 mg).

In this work, the compounds to be investigated qualitatively were analyzed by the method of TLC, using aluminum oxide as the sorbent. For a quantitative determination of the compounds studied we used the

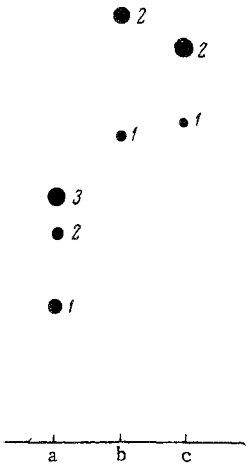


Fig. 1

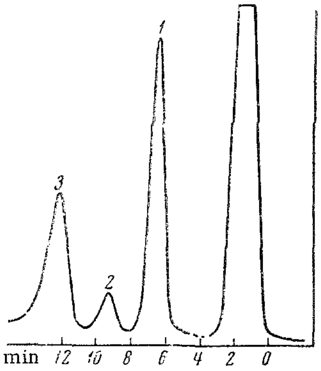


Fig. 2

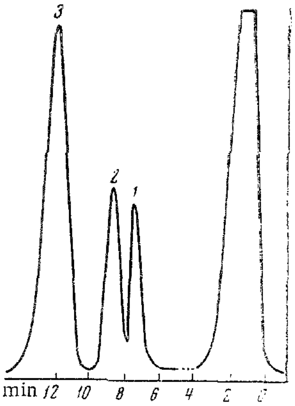


Fig. 3

Fig. 1. Chromatogram in a thin layer of Al_2O_3 of mixtures: a) R^1SR^1 (1), R^1SR^2 (2); R^2SR^2 (3); b) monoacetate of R^1SR^1 (1), diacetate of R^1SR^1 (2); c) monoacetate of R^2SR^2 (1), diacetate of R^2SR^2 (2).

Fig. 2. Chromatogram of a mixture of R^1SR^1, R^2SR^2, and R^1SR^2. Detector: flame-ionization, column temperature 190°, injection temperature 210°; 1) R^2SR^2; 2) R^1SR^2; 3) R^1SR^1.

Fig. 3. Chromatogram of a mixture of R^1SR^1, its mono- and diacetates. Detector: flame-ionization, column temperature 185°, temperature of doser 210°; 1) monoester of R^1SR^1; 2) diester of R^1SR^1; 3) R^1SR^1.

Institute of Chemical Physics, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1379-1383, July, 1971. Original article submitted September 4, 1969.

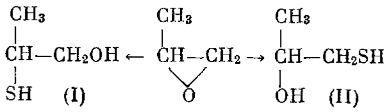
TABLE 1. R_f Values of Certain bis-(β-Hydroxyalkyl)-Sulfides, Their Esters, and β-Hydroxyalkyl Mercaptans

Substances	R_f
R^1SR^1	0,27
R^1SR^2	0,42
R^2SR^2	0,49
Esters of R^1SR^1, mono-	0,61
di-	0,84
Esters of R^2SR^2, mono-	0,63
di-	0,78
R^1SH	0,47
R^2SH	0,55

TABLE 2. Results of Analysis of bis-(β-Hydroxyalkyl)-Sulfides, Their Esters, and β-Hydroxyalkyl Mercaptans

Substances	Retention time, min	
	on polyethylene glycol adipate	on Apiezon-L
R^1SR^1	12,33	9,17
R^1SR^2	9,10	8,5
R^2SR^2	6,75	8,17
Esters of R^2SR^2, mono-	5,9	8,2
di-	6,9	11,1
Esters of R^1SR^1, mono-	7,15	7,55
di-	8,5	10,4
R^1SH	2,75	2,2
R^2SH	2,25	2,1

method of gas – liquid chromatography (GLC). We also analyzed the reaction products of H_2S with propylene oxide by the PMR method. In the reaction of H_2S with ethylene oxide, the basic products are β-hydroxyethyl mercaptan (R^1SH) and bis-(β-hydroxyethyl)-sulfide (R^1SR^1). In the interaction of H_2S with propylene oxide, depending on the site of cleavage of the C–O bond in propylene oxide, one of the two isomeric hydroxy mercaptans (I) or (II) (R^2SH), or both compounds simultaneously, can be formed



Analogously, three isomeric bis-(β-hydroxypropyl)-sulfides (R^2SR^2) can be formed. The compounds R^2SH and R^2SR^2, obtained in the reaction of propylene oxide and H_2S, were isolated from the reaction mixture by redistillation under vacuum and identified according to the boiling points and elemental chemical analysis. However, these methods did not give any information on the structure of the compounds.

Together with the PMR spectra of these compounds, we also obtained the spectra of R^1SH, R^1SR^1, as well as diesters of acetic acid with R^1SR^1 and R^2SR^2 under the same conditions.

EXPERIMENTAL

Thin-Layer Chromatography. Aluminum oxide, "second standard" brand, was used as the sorbent. The thickness of the aluminum oxide layer was 1 mm. Dimensions of the glass plate 13 × 17 cm. The mobile liquid was a mixture of ethanol and benzene, 1:9 (by volume). The concentration of the substances to be analyzed did not exceed 1% for the bis-(β-hydroxyalkyl)-sulfides and 0.1% for β-hydroxyalkyl mercaptans.

All the substances were developed with iodine vapors. In addition, in a number of cases qualitative reactions were used for the development of certain compounds. An aqueous alkaline solution of sodium nitroprusside was used for the qualitative determination of compounds containing a mercapto group [2]. Moreover, we established that alcohol solutions of copper nitrate and sulfate, used previously for the qualitative determination of bis-(β-chloroethyl)-sulfide [3], can be used for the qualitative detection of bis-(β-hydroxyalkyl)-sulfides. Moreover, in this case the best results were obtained with copper nitrate. The investigated compounds were detected using these reagents by spraying the damp plates from an atomizer immediately after separation of the components in a layer of aluminum oxide.

Table 1 presents the results of a chromatographic determination on aluminum oxide of bis-(β-hydroxyethyl)-sulfide, bis-(β-hydroxypropyl)-sulfide, β,β'-hydroxyethylhydroxypropyl sulfide (R^1SR^2), β-hydroxyethyl mercaptan, β-hydroxypropyl mercaptan, as well as esters of acetic acid with R^1SR^1 and R^2SR^2. R_f values of all the compounds were determined with an accuracy of more than 2%. From the data of Table 1 it is evident that the values of R_f, for example, for R^1SR^1, its mono- and diesters, vary according to the variation of their adsorption capacity, which decreases with the successive introduction of two ester groups into R^1SR^1, according to the general rules of [4].

TABLE 3. Values of the Chemical Shifts (ppm) and Spin–Spin Interaction Constants (Hz) of β-Hydroxyalkyl Mercaptans and the Corresponding Sulfides

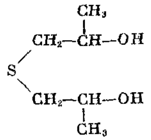
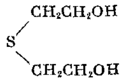
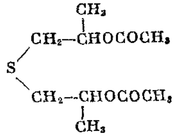
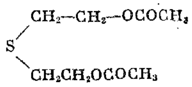
Formula	Solvent	δ_{SH}	δ_{S-CH_2}	δ_{O-CH_2}	δ_{C-H}	δ_{CH_3}	δ_{OCOCH_3}	δ_{OH}	$J_1;\ J_2$ J_{SH-CH_2}	J_3 $J_{CH_2-CH_2}$	J_{CH_2-CH} J_{CH_3-CH}
$HSCH_2CH(OH)CH_3$	CCl_4	1,50	2,51	—	3,74	1,19	—	4,25	7,7; 9,1	—	6,30
$HSCH_2CH_2OH$	CCl_4	1,61	2,64	3,60	—	—	—	4,54	7,45; 8,65	6,10	—
	C_6H_6	—	2,54	—	3,82	1,19	—	4,60	—	—	6,90
 $S(CH_2CH_2OH)_2$	D_2O	—	2,66	3,70	—	—	—	4,56	—	6,50	—
	CCl_4	—	2,56	—	4,86	1,23	1,94	—	—	—	6,14
 $S(CH_2CH_2OCOCH_3)_2$	CCl_4	—	2,71	4,10	—	—	1,96	—	—	6,65	—

Figure 1 presents chromatograms of three different mixtures of organosulfur compounds. The chromatogram *a* presents the results of an analysis of the products of the reaction of propylene oxide with H_2S in the presence of R^1SR^1. The chromatogram was developed for the detection of RSR.

The three bis-(β-hydroxyalkyl)-sulfides were identified according to the values of R_f and according to qualitative reactions (data of Table 1). The chromatograms b and c present the results of an analysis of the products of esterification of R^1SR^1 and R^2SR^2 by acetic acid. In this case, mono- and diesters of the corresponding RSR were detected in each mixture.

Gas – Liquid Chromatography. The investigated bis-(β-hydroxyalkyl)-sulfides and their esters with acetic acid are high-boiling liquids; these substances are thermally unstable. Thus, for example, R^1SR^1 decomposes at a temperature of 216°. These circumstances are responsible for the difficulty of selecting optimum conditions for analysis. It was found that the temperature of injection in the analysis of sulfides should not exceed 210°, since at a higher temperature false peaks appeared as a result of decomposition of the investigated compounds. The best temperature for the column proved to be 185°. In the analysis of β-hydroxyalkyl mercaptans, the optimum column temperature was 90°, temperature of injection 110°. Of the stationary phases that we investigated, the best proved to be polyethylene glycol adipate, which permitted the separation of all three bis-(β-hydroxyalkyl)-sulfides, as well as their mixtures with the corresponding mono- and diesters of acetic acid. The analysis was conducted on a Tsvet chromatograph, using a flame-ionization detector. The rate of flow of nitrogen was 125 ml/min, column length 1 m. The amount of the stationary phase was 15% of the weight of the solid carrier (Celite C-22).

The results of an analysis of the investigated compounds are cited in Table 2. Data obtained with polyethylene glycol adipate and Apiezon-L are cited for comparison; as can be seen from Table 2, the latter cannot be recommended for the analysis of the investigated mixtures. Figures 2 and 3 present chromatograms of a mixture of three bis-(β-hydroxyalkyl)-sulfides, as well as a mixture of R^1SR^1 with its mono- and diacetates. As can be seen from Table 2 and Figs. 2 and 3, a good separation of the initial components of these mixtures is observed on polyethylene glycol adipate.

PMR Spectra. The PMR spectra were taken at room temperature on a JNH-3H-60 spectrometer with a working frequency of 60 MHz. The samples for obtaining the PMR spectra were 50% solutions in CCl_4, C_6H_6, and D_2O; hexamethyldisiloxane was used as the internal standard, and for aqueous solutions dioxane. The scale of the chemical shifts was constructed in units of δ, ppm (relative to hexamethyldisiloxane). The spin – spin interaction constants (SSIC) were measured in a frequency development system with stabilization according to the working sample. The accuracy of measurement of the chemical shift was ±0.02 ppm, and the SSIC ±0.05 Hz.

The values of the chemical shifts and SSIC in the PMR spectra of the investigated substances are cited in Table 3. An analysis of the PMR spectra and the data of Table 3 supports the occurrence of the reaction of H_2S with propylene oxide with the formation of a β-hydroxy mercaptan and a dihydroxydialkyl sulfide with the sulfur atom at the primary carbon atom.

The authors would like to thank L. N. Naumova for her aid in conducting this work.

CONCLUSIONS

1. The possibility of a qualitative analysis of β-hydroxyalkyl mercaptans and the corresponding sulfides, formed in the interaction of ethylene and propylene oxides with hydrogen sulfide, by the method of thin-layer chromatography on aluminum oxide was studied. A method of detection of the spots of the compounds to be analyzed, using reagents giving qualitative reactions for mercaptans and hydroxyalkyl sulfides, was proposed.

2. A method was developed for the analysis of the reaction products of hydrogen sulfide with ethylene and propylene oxides, as well as esters of bis-(β-hydroxyalkyl)-sulfides and acetic acid, by the method of gas – liquid chromatography. The possibility of separating mixtures of the indicated compounds was demonstrated.

3. The structure of the reaction products of hydrogen sulfide with propylene oxide was established by the PMR method.

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