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Abstract

Full Text

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β-BUTYLTHIOPHANE ISOLATED FROM THE OIL OF THE COAL-BEARING SERIES OF THE TUIMAZY FIELD

(Presented by Academician I. N. Nazarov, 20 XI 1956)

Cyclic sulfides contained in petroleum fractions boiling above 200° have been studied very little. In Mabery' s investigations ([1]), published in 1906, the presence in the kerosene distillate of Canadian oil of compounds boiling above 200° and having the general formula $C_{nH_{2n}}S$ was established. These compounds were given the name thiophanes. However, not one of them was isolated in pure form and identified.

Up to the present time, researchers in various countries of the world have identified in petroleum products boiling above 200° only one cyclic sulfide, and it has been established that the cyclic sulfides contained in petroleum products may belong to various homologous series ([2–5]).

In view of the foregoing, it seemed of some interest to us to report on the β-butylthiophane that we isolated from the oil of the coal-bearing series of the Tuimazy field. This oil was subjected by us to vacuum isothermal rectification, during which the still temperature was constant and equal to $135 \pm 0.5°$, while the pressure was gradually lowered from atmospheric to 0.5 mm Hg. The entire apparatus was made of stainless steel and glass. As a result of the rectification, 2% by volume fractions were obtained, which, on distillation according to GOST, boiled within a range of 12-18°. One of these fractions, boiling within 196-214° and containing 1.02% total sulfur, was subjected to chromatography on MSM-grade silica gel. For this purpose, silica gel having a grain size of 0.5-0.25 mm was charged into a brass chromatographic column 4.5 m high and 18 mm in diameter. The silica gel was then completely wetted with the fraction being chromatographed, after which it was washed with acetone. In the course of the chromatography, three chromatographic filtrates were collected. Filtrate I was a mixture of paraffinic and naphthenic hydrocarbons, containing no organosulfur compounds. Filtrate II—intermediate—was a product in which the total sulfur content was 1.31%. Filtrate III, after the acetone had been distilled off from it, was a mixture of aromatic hydrocarbons and organosulfur

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Fig. 1. Absorption spectrum of β-butylthiophane in the ultraviolet region (in isooctane solution)

Figure 1: Fig. 1. Absorption spectrum of β-butylthiophane in the ultraviolet region (in isooctane solution)

compounds. The content of total sulfur in it was 9.10%; moreover, this filtrate contained 68.6% of the sulfur, calculated on the sulfur present in the fraction taken for chromatography.

Filtrate III was subjected to repeated chromatography under the same conditions as the 196–214° fraction. As a result, two chromatographic filtrates were isolated. The content of total sulfur in I was 6.10%, and in II 14.0%; moreover, filtrate II contained 49.5% of the sulfur, calculated on the sulfur present in the 196–212° fraction. Filtrate II was then dissolved in isooctane and subjected to further chromatography in a column 1 m high and 10 mm in diameter, filled with ShSM-grade silica gel. The eluent in this case was a mixture of benzene and acetone, taken in a ratio of 1:1 by volume. In the course of chromatography, five filtrates were collected, from which the eluent was then distilled off in vacuo, and in each of them

the content of total sulfur was determined. Filtrate V contained 22.4% total sulfur, which, recalculated to the sulfur contained in the 196–214° fraction, amounted to 11.3%.

Filtrate V from the third chromatographic separation was subjected to vacuum distillation. For the distillate, the specific gravity, refractive index, molecular weight, and elemental composition were determined (by the semimicro method). The content of sulfide sulfur, determined by the method of potentiometric titration, proved to be equal to the sulfur content obtained by elemental analysis. In addition, a combination-scattering spectrum was obtained (on an ISP-51 spectrograph), and an absorption spectrum (in a solution of standard isooctane) in the ultraviolet region (on an ISP-22 spectrograph)*. The spectra were photometered on an MF-2 microphotometer and measured on an IZA-2 comparator. The absorption spectrum of the isolated compound in the ultraviolet region is shown in Fig. 1. In the literature available to us we have not encountered data on the absorption spectrum of β-butylthiophane in the ultraviolet region.

Fig. 1. Absorption spectrum of β-butylthiophane in the ultraviolet region (in isooctane solution)

The following characterization of β-butylthiophane attests to the identity of the organosulfur compound isolated by us from the oil of the coal-bearing suite of the Tuimazy field and β-butylthiophane synthesized by Yur' ev ([6]).

(d_4^{20}) 0.9260 (lit. ([6]) 0.9271); (n_D^{20}) 1.4869 (lit. ([6]) 1.4868); molecular weight: found 144, calculated 144.27; b.p. 210°/760 mm (lit. ([6]) 209.5-209.9°/733 mm); (R_D): found 0.3105, calculated 0.3101.

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Line in the combination-scattering spectrum characteristic of the thiophane ring (( )) 687 ± 3 cm(^{-1}) (lit. ([6]) 690 cm(^{-1})).

Found (wt. %): C 66.55; H 11.22; S 22.4
Calculated (wt. %): C 66.59; H 11.18; S 22.23

Sulfide sulfur, determined potentiometrically (wt. %): found 22.4; calculated 22.23.

It should be noted that β-butylthiophane was isolated by us from oil only with the aid of vacuum rectification and chromatography, whereas all sulfides described in the literature, which had been reported as found in petroleum products, were isolated through complex compounds of mercury salts.

The β-butylthiophane identified by us is the second cyclic sulfide isolated from petroleum that boils above 200°.

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* The combination-scattering spectrum was obtained by A. D. Biktasheva, and the spectrum in the ultraviolet region by N. S. Lyubopytova.

Note: Figure translations are in progress. See original paper for figures.

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