

Carboxylic Acids in the Products of Hydrothermal Decomposition of Barzassite

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(Received October 30, 2002)

Abstract

The results of the experiment on hydrothermal decomposition of Barzas sapromixite aimed at obtaining carboxylic acids are reported and discussed. Normal mono- and dicarboxylic acids with 9 to 25 and with 10 to 23 carbon atoms, respectively, were identified in decomposition products. The yield of carboxylic acids from sapromixite turned out to be 2–4 times lower than for the majority of sapropelites investigated earlier.

INTRODUCTION

Mixtures of carboxylic acids are widely used in the production of synthetic rubber and plastics, emulsifiers and special compositions for food industry, metallurgy, machine-tool construction, motor-car construction, they are also used to make drilling fluids [1]. Small-scale production of mixtures of carboxylic acids from sapropelite coal and shale oil can be economically reasonable in some regions [2]. Previously we demonstrated [3–6] the possibility to achieve high yield (up to 60 %, calculated for the organic mass of coal) of carboxylic acids by means of hydrothermal decomposition of Siberian sapropelites. The goal of the present work is to investigate the Barzas sapromixite coal as a possible raw material for obtaining synthetic acids, which is especially urgent for the regions devoid of any deposits of sapropelite coal and shale oil suitable for processing (for example, the Kuznetsk Basin).

EXPERIMENTAL

The sample of the Barzas coal was collected near the Barzas settlement (Kemerovo Dis-

trict) from a bore pit 5 m deep. The coal sample consists of fine dim dark-brown (sometimes black) films less than 1 mm thick; some of them are pressed and oriented in different directions with respect to each other. Numerous oblong three-layered stripes are observed with a microscope in the vertical sections; the two outer layers are yellow, well luminescent with yellow colour; the inner layer is red and non-luminescent. In the cases when the stripes fit each other closely, the outer yellow layers merge each other. The coal sample is an accumulation of pressed thin stems of psilophytes with predominance of yellow thick cuticles. Vitrinite lying between the cuticles comprises the inner part of stems. The Barzas coal belongs to the cuticular liptobioliths and is composed of lipinitite and vitrinite.

Elemental analyses of the barzassite samples were made in the Laboratory of Microanalysis of the Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS.

Before investigation, the samples of coal were ground with a washer mill until the entire sample could be bolted through a 0.2 mm sieve.

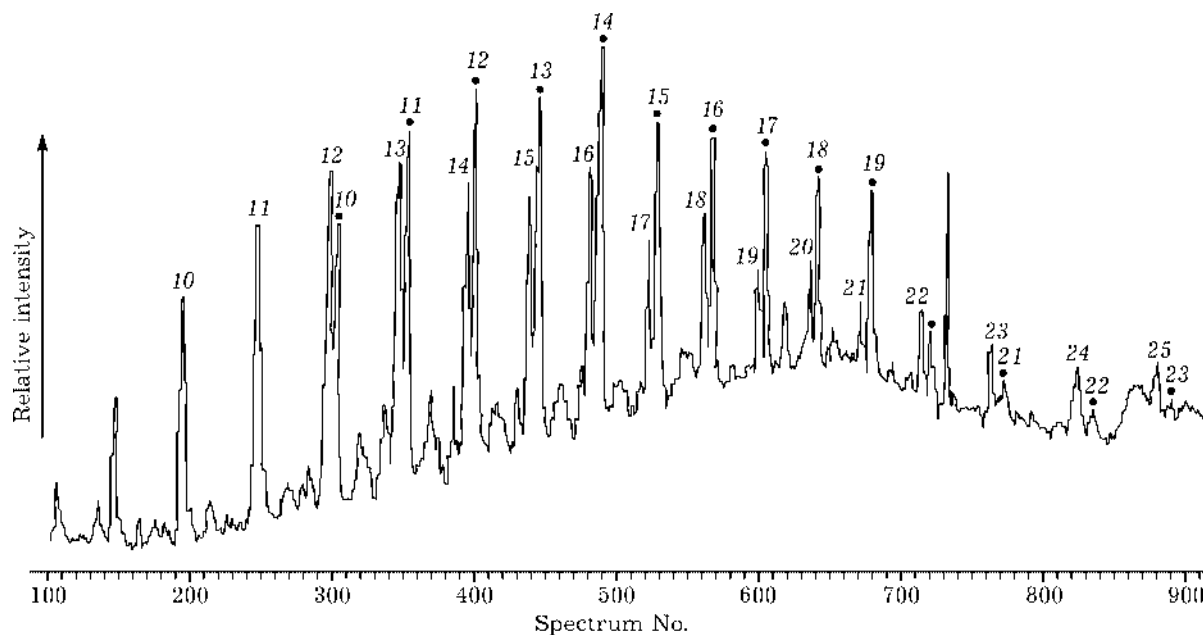


Fig. 1. Mass chromatogram of methyl esters of the carboxylic acids from the products of hydrothermal decomposition of barzassite (numerals and numerals with points above peaks mean the number of carbon atoms in mono- and dicarboxylic acids, respectively).

Hydrothermal decomposition of barzassite was carried out in a rotating autoclave made of 1Cr18Ni10Ti (1Kh18N10T) steel 0.5 l in volume, equipped with a thermocouple, high pressure valve and a manometer. The autoclave was charged with 10 g of the sample, 300 ml of a 5% KOH solution, gaseous nitrogen (5 MPa) and heated while rotating (200 rpm) in an electric furnace for 50–60 min to a temperature of 400 °C. Temperature in the autoclave was maintained with an accuracy of ± 2 °C at the required level for 1 h and recorded in the coordinate paper. Pressure in the autoclave was measured with the manometer to 4%. Then the autoclave was cooled to 40 °C with compressed air and discharged. The liquid and solid products were taken out of the autoclave and passed through a glass filter; the precipitate remaining on the filter was washed with diethyl ether (150 ml). The procedures of isolation and methylation of carboxylic acids were described in [7].

Gas chromatographic-mass spectrometric analysis of the mixtures of methyl esters of carboxylic acids was carried out with the LKB-2091 instrument with DS-2130 treatment system. The column was a capillary 35 m long with the inner diameter of 0.25 mm; immobile phase

was dimethylsiloxanesilarylenic copolymer (DMSSAS), the temperature of the column was 50 (8 °C/min)–360 °C, separator: 330 °C, carrier gas was helium. The energy of ionizing electrons was 70 eV.

RESULTS AND DISCUSSION

Two homologous groups were revealed in the mass chromatogram (Fig. 1) of methylated compounds: methyl esters of normal monocarboxylic acids (I) and dimethyl esters of normal dicarboxylic acids (II). Some representatives of these groups [for example, $\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$ (I), $\text{CH}_3\text{OOC}(\text{CH}_2)_7\text{COOCH}_3$ (II)] were identified with the help of the searching system [8]. In addition, the spectra of the corresponding groups of compounds have rather general appearance allowing one to reveal their characteristic indices. For instance, for the spectra of group I, characteristic peaks of ions with $m/z = 74$, 87, 43 and the peaks of ions $[\text{M}-43]^+$, $[\text{M}-31]^+$, $[\text{M}-29]^+$ are observed, while for the spectra of group II $m/z = 74$, 55, 98 and $[\text{M}-73]^+$, $[\text{M}-64]^+$, $[\text{M}-31]^+$, which is in good agreement with the data reported in [9, 10].

TABLE 1

Comparative characteristics of coal samples and the yield of carboxylic acids after hydrothermal decomposition

Basin, deposit	A^d	Elemental analysis, %				Petrographic analysis, %			Yield of carboxylic acids, % of coal mass
		C^{daf}	H^{daf}	S^{daf}	N^{daf}	A	V	L	
Kuznetsk, Barzas	15.3	79.4	9.7	0.5	0.5	0	11	89	10
Lena, Taimylyr	3.5	82.6	9.5	0.3	0.7	87	13	0	20 [4]
Lena, Charchik	3.6	84.0	10.1	0.3	0.4	73	27	0	28 [5]
Irkutsk, Budagovo	10.4	81.4	10.3	0.2	1.2	90	10	0	25 [5]
Kansk-Achinsk, Sobolevo	25.4	70.3	10.2	0.3	0.9	73	27	0	39 [5]

Note. A^d is ash content calculated for the dry mass of coal; daf (dry ash free) – calculated for the dry ash-free coal mass; A – alginite, V – vitrinite, L – liptinite.

In addition, one may see in Fig. 1 that monocarboxylic acids (4.6 %) have the range of distribution C_9-C_{25} with a maximum at C_{11} . For dicarboxylic acids (5.4 %), the number of carbon atoms in the molecule varies from 10 to 23 with a maximum at C_{14} . Along with these acids, other carboxyl-containing compounds are also present; their identification is hindered due to the absence or weak intensity of molecular ions in the spectra.

The yield of carboxylic acids from the products of hydrothermal decomposition (Table 1) in the case of barzassite is 2–4 times lower than for sapropelites investigated earlier.

Theoretical provisions describing the formation of sapropelite kerogen allow one to make assumptions concerning the composition and structure of the products of its hydrothermal decomposition [7]. Thus, b-carbonyl and (or) hydroxyl groups in the structures of sapropelite kerogen under the conditions of hydrothermal decomposition are subjected to hydrolytic splitting over the most polarized carbon-carbon bonds with the formation of oxygen-containing compounds, mainly aliphatic mono- and dicarboxylic acids of normal structure. One cannot exclude that the kerogen of barzassite also contains these structures but their amount is smaller. In the case under consideration, aliphatic carboxylic

acids are likely to be formed from polymerlipidolipoids but not from polymerlipids comprising sapropelite kerogen [11]. Petrographers insist [12, 13] that the kerogen of barzassite has psilophyte nature and cannot be related to sapropelite formations. In the opinion of the authors of [14], the Barzas coal does not belong to sapropelite but mainly is composed of special lignins similar in composition with the lignins of modern laminaria, representatives of highly organized brown kelp. These cuticular organisms were growing in littoral shallow water of the continental intermittent lagoon water reservoirs which existed under the conditions of arid climate [15].

CONCLUSIONS

On the basis of the results obtained, we may assume that the Barzas sapromixite coal, unlike sapropelite coal, cannot be considered as a promising raw material for obtaining synthetic carboxylic acids because of their low yield. The main structural elements of barzassite are likely to be inherited from the lipid material of higher plants but not from the lipids of algae and other microorganisms (as it is the case with sapropelite kerogen formation). This is evidenced

by the results of petrographic and chemical investigations. By the present moment, exceptional originality of the microstructure and composition of this coal is of interest only for geochemists.

Acknowledgement

The authors thank Dr. Sci. in Chem. V. N. Sidel'nikov (Boreskov Institute of Catalysis, SB RAS, Novosibirsk) for encouragement of carrying out gas chromatomass-spectrometric examination of the products of hydrothermal decomposition of sapromixite coal.

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