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Composition of Products Obtained *via* Kashpir Deposit Shale Oil Ozonization in Chloroform

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Abstract

Process features and the component composition of the products of ozonolytic destruction of the shale oil kerogen from the Kashpir deposit in the Volga Basin were studied. The products soluble in chloroform and water are represented by sulphuric acid, *n*-dicarboxylic aliphatic acids C_2–C_{14}, keto acids and the acids of branched structure, whose amounts are quite comparable. Water-insoluble compounds include higher fatty acids C_{10}–C_{18}, benzenedicarboxylic acids, as well as keto and oxy forms of aromatic (including hydroaromatic and nitrogen containing) compounds.

Key words: ozonization, kerogen, sulphur-bearing shale oil

INTRODUCTION

Liquid phase ozonization represents one of efficient methods for the destruction of high molecular organic substance (OS) of combustible minerals (CM) to yield readily analyzed low molecular components reflecting the features of the structure of initial plant material. Most actively the mentioned method was started to apply since the second half of the last century for studying the structure of kerogens from shale shale oil (SO) and with the purpose of obtaining oil-replacing raw material on their basis [1–3]. So, the authors of [4, 5], basing on the analysis of the composition of ozonization products (*n*-mono- and *n*-dicarbonic, lactonic and methoxy acids) resulted from the kerogen of the Boltysh, Green River, Gdov SO in an glacial acetic acid concluded on a mainly aliphatic character of their structure, whose fragments therein are bonded by multiple carbon-carbon and ester-like bonds. Thus it was marked [4, 5], that the Kashpir SO exhibits an abnormal behaviour under the conditions of ozonolysis, whereas the products of its oxidation differ in composition from the products obtained from shale oil species from other deposits. However, the authors of the mentioned papers do not present any detailed analysis of oxygen-containing fractions isolated from the Kashpir of shale oil.

The analysis of both our own data [6, 7] and data from the literature [1–5] revealed a considerable difference in the intensity processes and the structure of products under CM ozonization in various solvents. We established that a stepwise ozonization process in neutral solvents (for example, chlorinated alkanes) with the subsequent extracting a residual sample by an oxygen-containing solvent is a more optimum one from the standpoint of conserving the carbon skeleton of CM OS fragments under extraction. An increase in the ozone solubility in acetic acid and, as a consequence, the increase in ozone concentration in the reaction mixture (approximately, three fold) results in the development of destructive oxidation processes and the loss of selectivity inherent in ozonolytic reactions.

The purpose of the present work consisted in studying the features of the process and the composition of products for the ozonization of sulphurous shale oil from the Kashpir deposit.

EXPERIMENTAL

As a subject of inquiry, we chose SO kerogen from the Kashpir deposits of the Volga pool. Kerogen (ash level A^d = 13.5 %) was obtained by means of the serial processing of a SO sample (A^d = 70 %) by the solutions of diluted hydrochloric acid and hydrofluoric acid. Demineralised SO was extracted by chloroform for removing bituminoid.

The ozonization was carried out at a room temperature in the suspension of kerogen (fraction <0.063 mm, a weighed portion equal to 2 g) in chloroform. The rate of feeding the ozone-oxygen mixture was equal to 160 mL/min, the concentration of ozone amounting to 1–1.2 vol. %, the duration of one ozonization cycle being of 5 h. The products formed were divided into ones soluble in chloroform (CHS), soluble in acetone and the solid insoluble residue. The products soluble in acetone, in turn, were divided into water-soluble (WS) products and water-insoluble (WIS) products.

In order to characterize samples we used data resulted from the elemental analysis, chemical functional analysis, IR spectroscopy, chromatography mass spectrometry.

The amount of carbonyl, oxygen-containing groups was determined according to the reaction with hydroxylamine chloride, the amount of carboxylic groups was determined by the acetate method, whereas the sum of carboxylic and hydroxyl groups was determined basing on ion exchange with sodium hydroxide. The content of oxygen in the "active" form as the sum of its amount as phenolic, carbonyl and carboxylic groups, that in the "inactive" form was calculated as a difference between the total content of oxygen and the oxygen content in the "active" form.

Diffusion reflection IR spectra were registered using a Bruker Tensor-27 FT-IR spectrometer. The chromatography-mass spectrometry analysis was carried out on an Agilent 19091S-433 chromatograph within the range of 15–500 amu; HP-5MS capillary column (5 % diphenylsiloxane, 95 % dimethylsiloxane) 30 m × 0.25 mm × 0.25 μm; helium was used as a carrier gas. Chromatographed products were preliminary methylated by diazomethane in diethyl ether.

RESULTS AND DISCUSSION

The analysis of the results describing the process of ozonization (changing in elemental composition, the accumulation dynamics of oxygen-containing groups, the group composition of soluble products), revealed a high level of interaction with ozone for the OS of Kashpir SO (Fig. 1) than for the CM of sapropelite nature investigated earlier [6, 8].

The increase in the content of identified oxygen-containing groups (carbonyl, carboxylic, phenolic) due to the ozonolysis of the Kashpir SO is caused by a considerable extent by the participation of "inactive" oxygen forms (ether, lacton, *etc.*) in the course of oxidation (see Fig. 1). The greatest increase corresponds to carbonyl groups whose content in the OS shale oil exhibits a five-fold increase after 3 h of ozonization.

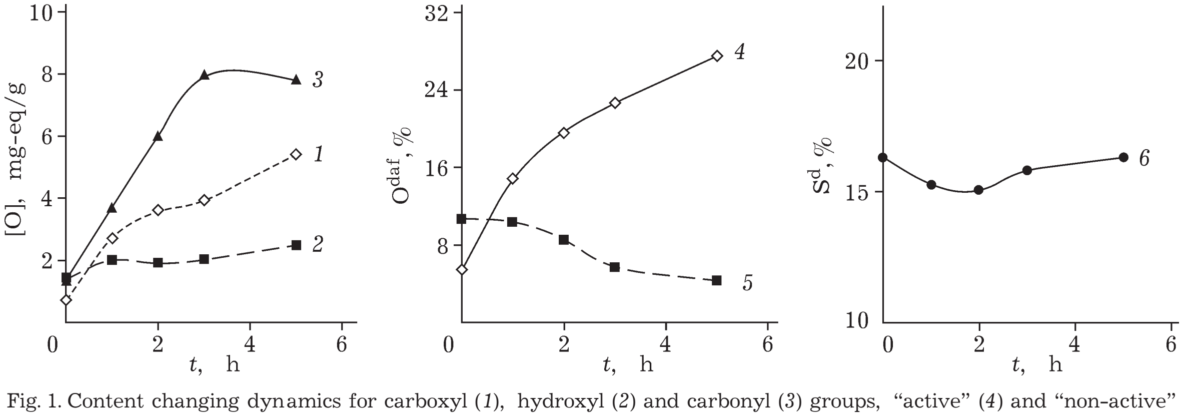

Fig. 1. Content changing dynamics for carboxyl (*1*), hydroxyl (*2*) and carbonyl (*3*) groups, "active" (*4*) and "non-active" (*5*) oxygen as well as total sulphur (*6*) in the Kashpir shale oil kerogen after its ozonization in chloroform.

TABLE 1

Characteristics of the Kashpir shale oil kerogen and the products of its ozonization

Products	Yield, mass % daf	Carbon fraction in products, % from initial	Ash level (A^d), %	Elemental composition, % daf			H/C	Functional composition, mg-eq/g		
				C	H	S		COOH	OH	CO
Initial kerogen	–	100	13.5	59.9	6.7	16.3	1.34	0.69	1.37	1.36
Insoluble residue	64.3	53.4	15.4	49.7	5.9	11.6	1.42	4.58	3.70	5.0
Soluble in chloroform	6.7	5.6	0.2	49.9	6.7	n/d	1.61	8.31	3.00	6.75
Soluble in acetone Including:	53.3	34.3								
water-soluble	36.0	18.8	10.0	31.3	5.0	9.0	1.91	10.99	3.83	6.42
water-insoluble	17.3	15.5	2.6	53.5	7.3	n/d	1.64	3.03	3.70	5.72
Total	124.3	93.3								

Note. n/d – not determined due to small yield of a product.

The amount of the total sulphur in the solid residue with ozonizing the kerogen tends to reduce at the initial stage of the process (see Fig. 1), but then it reaches the initial values. This fact could be connected with the increase of the fraction of inorganic sulphur due to the removal of organic components of shale oil in the form of soluble products in chloroform.

For obtaining the products of oxidation, we restricted ourselves to three cycles (15 h) converting about 40 mass % of shale oil OS into the soluble state. In this case, from the initial kerogen 39.9 % of carbon converted into the soluble form, 6.7 % of that converted into gaseous and volatile products, and 53.4 % of carbon converted into the insoluble residue (Table 1). Thus, it should be noted that the ozonization of the Kashpir SO in the chloroform medium was carried out with insignificant OS loss with gaseous products.

One of distinctive features inherent in the ozonization of sulphurous Kashpir SO consists in a high content of WS substances (see Table 1). At the same time, the products of SO ozonization from other deposits more often contain prevailing high molecular WIS substances, which is in a good agreement with the concepts that the sapropelite OS is composed of the products of polymerization of higher fatty acids [1–5]. To all appearance, an atypical behaviour observed for the Kashpir SO under the conditions of ozonolysis could be caused by the influence of abnormal hydrochemical mode with a high content of sulphate ions upon the formation of the fatty shale-forming material [9, 10].

Indeed, the content of sulphur (mainly, organic species [9, 10]) in the initial kerogen amounted to 16.3 %; a part of sulphur is distributed over soluble ozonization products of (see Table 1). The IR spectrum of kerogen exhibits wide bands corresponding to the IR absorption of C–S bonds (570–710 cm^{-1}) and C=S bonds (1030–1200 cm^{-1}), which indicates the presence of sulphur heteroatoms in the organic matrix of kerogen in the structure of thiophenes, thiones and sulphide bridges. The IR spectra of WS and WIS products (Fig. 2) demonstrate narrower bands of C–S bonds (530–580 cm^{-1}), S–O bonds (850–900 cm^{-1}) and S=O bonds (1015–1060 cm^{-1}). These bands exhibit the greatest intensity in the IR spectrum of WS substances, which indicates a high concentration and uniformity of the structure of sulphur-containing soluble compounds those are present in among the products in oxidized form. Using the method of chromatography-mass spectrometry, soluble sulphur compounds, were identified as dimethylsulphate (the product of sulphuric acid esterification by diazomethane), whose content in WS products amounted up to 25 %.

The absence of other soluble sulphur species (sulphones, sulphoxides) indicates predominantly ozone destructing the fragments containing thione groups those can be oxidized with the abstraction of a sulphur atom [11] to give sulphuric acid. A high content of sulphur (to all appearance, thiophene sulphur) in the solid insoluble residue after the extraction of soluble products can serve as a confirmation of this assumption (see Table 1).

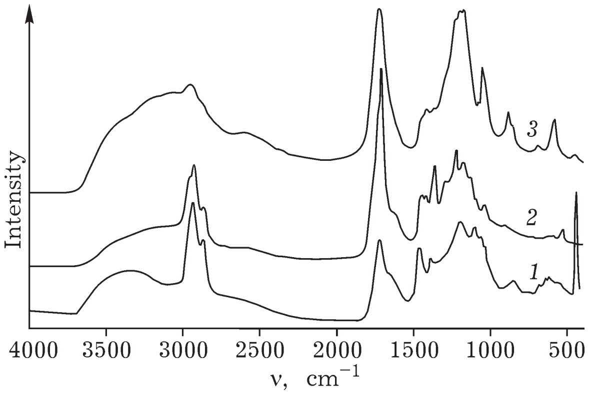

Fig. 2. IR spectra of the Kashpir shale oil kerogen (*1*), water-insoluble (*2*) and water-soluble (*3*) products of its ozonization.

Among oxygen-containing CHS and WS Kashpir SO ozonization products chromatographed one can observe prevailing (48 and 62 mass %, respectively) dimethyl esters of inherent in kerogen destruction C_2–C_{14} *n*-dicarboxylic aliphatic acids (*n*-DCA) with the maximum of distribution at C_4–C_6 (Table 2). A low content of higher DCA (0.2–1.5 %) inherent in SO from other deposits [4, 5, 7] in the products, to all appearance, could be connected with changes in the composition of initial fatty material under the conditions fossilization in sulphur-containing environment [9, 10]. In this case, the occurrence of oxalic acid (7 % in CHS and 18 % in WS substances), usually absent among the products of CM ozonization in chloroform [6, 8], could be caused by a catalytic influence upon the process of sulphate ion oxidation (the destruction product of sulphur-containing organic fragments).

The esters of *n*-monocarboxylic acids (*n*-MCA), whose formation could be connected with the breaking of peripheral alkyl groups by ozone from the macromolecules of kerogen, are contained in much smaller amounts (1–3 %) in the products and they have a long chain (C_{10}–C_{18}). One more feature of the products of the ozonolytic destruction of the Kashpir SO consists in a rather high total content of aliphatic acid esters with branched carbon skeleton, keto acids and tricarboxylic acids (see Table 2). The investigations carried out earlier [4, 5] concern-

TABLE 2

Componential composition of chromatographed esterified products of the Kashpir shale oil kerogen ozonization

Products	Mass fraction, %	Products	Mass fraction, %
Soluble in chloroform		2-Hydroxy-4-methoxy-BCA	0.4
Dimethylsulphate	5.6	Dimethyl esters:	
Methyl esters:		*n*-DCA C_2–C_{10}	48.8
n-MCA C_{12}, C_{13}, C_{15}	3.2	*n*-oxo-DCA C_7	1.1
n-oxo-MCA C_5	2.2	*iso*-DCA C_3–C_7	4.8
iso-MCA C_{13}, C_{15}, C_{17}	4.6	Trimethyl esters	
Dimethyl esters:		of tricarboxylic acids C_3, C_4	0.9
n-DCA C_2–C_{14}	62.8	*Total*	85.1
n-oxo-DCA C_7	2.9	**Water-insoluble**	
iso-DCA C_5–C_7	6.8	Methyl esters *n*-MCA C_{12}–C_{22}	21.5
Total	88.1	Dimethyl esters of BCA	2.6
Water-soluble		Methyl esters of methoxy-BCA	4.2
Dimethylsulphate	24.9	Oxohydroaromatic HC	4.8
Methyl esters:		Alkylaromatic HC	3.8
n-MCA C_{10}, C_{11}, C_{16}, C_{18}	1.0	Hydroaromatic HC	5.8
n-oxo-MCA C_4	1.9	Oxoalkenes	2.2
n-Hydroxy-MCA C_3	0.7	Nitrogen-containing aromatic HC	4.1
iso-MCA C_4	0.6	*Total*	49.0

Note. MCA – monocarboxylic aliphatic acids, DCA – dicarboxylic aliphatic acids, BCA – benzenecarboxylic acids, HC – hydrocarbons.

ing the products of the Kashpir SO ozonization did not revealed this fact (except for a high content of α- and β-methylglutaric acids).

About a half of chromatographed components of a more high molecular WIS fraction is presented by methyl esters of higher *n*-MCA $C_{11}-C_{22}$ (see Table 2) with a pronounced prevalence of palmitic acid C_{16} (10.5 %) and stearic acid C_{18} (5.8 %), which indicates that there is a contribution of a fatty component in the formation of the shale oil OS. Another part of WIS substances is presented by the destruction products of relatively large fragments of kerogen macromolecules, whose formation could be connected with a humus component.

Among them there are the esters of mono- and dicarboxylic aromatic acids with the number of benzene rings from one up to three, oxo and oxy species of hydroaromatic (hydroanthracene, hydrophenanthrene, hydrofluorene, dicyclopentabenzene, *etc.*), nitrogen-containing (chinoline, benzylamine, indole, nitroanthrafurane) and alkylaromatic compounds. The presence of nitrogen-containing compounds in a high molecular WIS fraction represents an evidence for the stability of nitrogen heteroatoms with respect to the impact of ozone molecules and their inclusion into a kerogen matrix within heteroaromatic structures.

CONCLUSION

Thus, basing on the composition of ozonization products of SO kerogen from the Kashpir deposit in chloroform (sulphuric acid, aliphatic acids of normal and branched structures, aromatic acids, oxo, oxy, alkyl- and hydroaromatic hydrocarbons), assumptions were confirmed [4, 5] concerning a considerable contribution of OS from organosulphuric and hydroaromatic components formed under the influence of the specificity of paleogeographic and geochemical factors responsible for the accumulation of the Volga pool shale-forming substance, to the structure of the compound under consideration [9, 10].

Taking into account the features of the fragmentary composition of the OS resulted from the Kashpir shale oil MP, one could believe that ozonolysis could simultaneously impact several types of groups and bonds such as multiple carbon-carbon bonds in aromatic (hydroaromatic) structures and in long alkyl chains, bonds between carbon, sulphur and oxygen heteroatoms, as well as saturated cycles with a high content of carbon tertiary atoms [11]. To all appearance, the presence of fragments with close reactivity with respect to ozone in the structure of the Kashpir shale oil kerogen can determine a high yield of soluble products under insignificantly developed processes of gas formation. At the same time, a catalytic influence is quite probable upon the oxidation of sulphate ions present in the reaction medium. To all appearance, thereof oxalic acid atypical for the reaction medium (chloroform) used appears in among the products of ozonization.

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