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ON THE STRUCTURE AND FORMATION OF BULGARIAN OIL SHALE KEROGEN

PART I. SOME CONCLUSIONS ON THE KEROGEN STRUCTURE BASED ON THE RESULTS OF THERMAL DEGRADATION

Abstract

Thermal degradation of kerogen under mild conditions, in an inert medium and under vacuum has been examined. The resulting products — gas, water, oil, semi-coke — have been analyzed applying a great number of physical and chemical methods of analysis. A complete material balance of the process has been done. Basing on the supposition that from one average fragment of the kerogen structure one mole of asphaltenes is removed it was estimated that 4.5 moles of resins, 2.85 moles of biaromatics with $R_{av} = C_{10}$, 2.34 moles of monoaromatics with $R_{av} = C_{18}$, 4.9 moles of alkanes C_{23} in average, etc. are removed along with one mole of asphalthenes. The number of the atoms in the given fragment is calculated from these results. It is demonstrated that the number of aromatic carbon atoms is 50 % — i.e. kerogen is of a high degree of aromatization and cyclization. It contradicts the results obtained during kerogen oxidation with $KMnO_4$ that gives a high yield of straight-chain dicarbonic acids. This difference in the results is explained. The heteroelements are supposed to have a strong influence on the process of kerogen structure formation.

Introduction

The organic parts of oil shale — both the solvent-extracted (so-called bitumes) and non-extracted (so-called kerogen) ones — have served as objects of a long-time examination. Though the bitumen composition of a large number of oil shales from various fields has been studied in practice, there exist quite different opinions about the kerogen structure [1—9]. Kerogen is the basic component of the oil shale organic matter. The elucidation of its structure is an important problem. Only then numerous theoretical and applied questions would be answered and some information on the genesis of oil shales and probably on that of the petroleum could be received. It is also important to bear in mind that oil shales are a large reserve of industrial carbonic raw material for the near future.

Kerogen of various fields significantly varies in structure and character ascertained mainly by the difference in its thermal degradation products. The basic difference in the kerogen structure probably rests not only on its carbon part as accepted by many researches but on the oxygen-containing part as well. Such a statement is supported, for example, by the fact that at thermal degradation of kerogen from Estonian oil shale a great quantity of phenols and neutral oxygen compounds are formed [4, 10]. There is an insignificant quantity of oxygen compounds in the oil from Bulgarian oil shale degradation despite the higher oxygen content of its kerogen. At the degradation it separates mainly as water, carbon dioxide and carbon oxide as will be demonstrated in the present report.

Theoretical

Generally two basic types of methods — physical and chemical one — are used for studying the kerogen structure. The physical instrumental methods of analysis do not cause any changes in the structure of the object under examination and consequently give more objective information. Unfortunately, they are of a considerably limited application and do not give enough information about the examined structure. By means of these methods, the presence of three-, four-, and in some cases eight-ring structures mainly of steroid type has been proved [3]. Recently, precise X-ray studies have shown a certain order in the structure of the examined kerogens and the respective X-ray structural indexes have given the possibility to determine the type of the ordered structures. Based on such data, ordered structures of long-chain hydrocarbons are proposed for one type of oil shale and aromatic structures for the other [11].

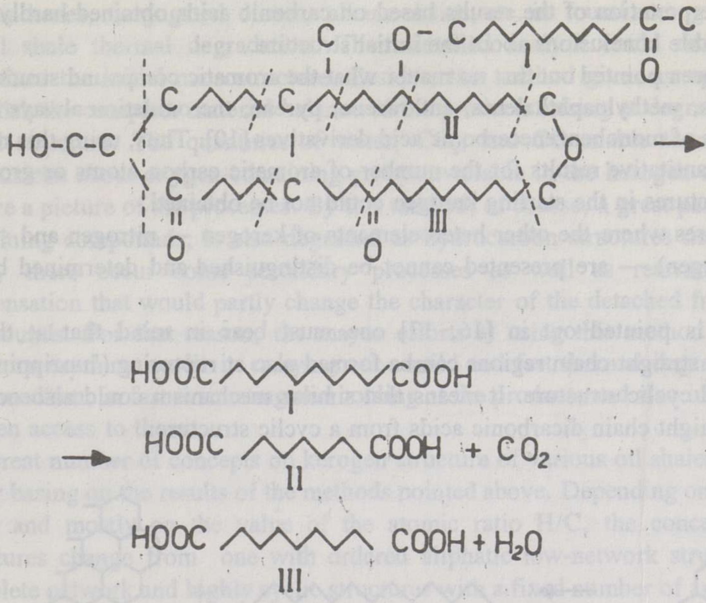
The second basic method of studying the structure of kerogen is its degradation to single fractions that could be examined easier than the whole structure. Suppositions about the macrostructure the fragment structures come from could be made. Usually the degradation takes place in two ways — a mild oxidative degradation and a mild thermal degradation.

The oxidative degradation takes place at temperatures from 20 °C to 90 °C under the influence of different kinds of oxidizers. Most often potassium permanganate in an alkaline medium, ozone, nitric acid, etc. are used [12—15]. Generally, at this method the organic part of oil shale is transformed into straight-chain dicarbonic and monocarbonic acids of different lengths from C_2 to C_{33}. Benzene carbonic acids of short chains are also formed, usually in insignificant quantity. It is accepted that the dicarbonic acids are formed when straight-chain regions at the both ends of the rupture are linked to other structural units. Monocarbonic acids are supposed to result from polymethylene chains linked only at one end to some other structural unit, the second end being free. They are assumed to indicate the presence of branched structures. It is accepted that benzene carbonic acids are obtained at oxidation of aromatic structures [4, 10, 12]. The yield of acids obtained could indicate the respective straight-chain, branched, and aromatic parts of the general kerogen structure.

Despite their wide application the methods of oxidation have been criticized for a great number of accompanying disadvantages. The more significant ones are:

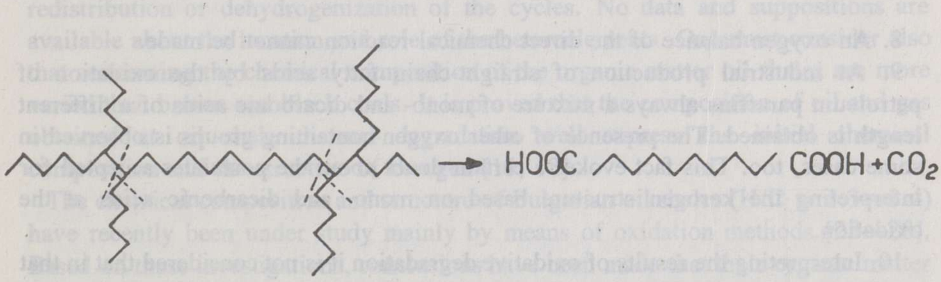
1. All kinds of oxygen-containing groups in kerogen are oxidized to carboxylic groups, CO_2, and H_2O, irrespective of the location of oxygen atoms — in a ring, in a straight chain, etc. So, this method could probably give some estimate only for the hydrocarbon part of the structure. However, at an usual atomic ratio $C/O = 6—10$ (i.g. one oxygen atom per every 6 to 10 carbon atoms) the conclusions basing on the results of kerogen oxidation are obviously indefinite, conditional and incomplete. It is due to the fact that by means of this method a difference between straight-chain and cyclic, non-oxygen and oxygen-containing, more simple or more complex structures could not be made. The example given below illustrates the impossibility

to give a correct interpretation of a model structure of a fragment from kerogen based on its oxidation products: most probably after the oxidation the regions I, II, III of the initial structure would be identified as the respective dicarbonic acids. (The length of dicarbonic acids is an approximate one.)



(1)

2. Straight-chain part could result from a branched region limited by two tertiary C-atoms:



(2)

3. At oxidizing the Estonian oil shales practically no benzene-carbonic acids are formed. On the other hand the oil obtained at this oil shale degradation contains a great number of phenols of various structures [4, 10, 18]. Thus, there appears a discrepancy between the conclusions about the presence or absence of aromatic part in the kerogen of these oil shales based on the results of oxidative and thermal degradation.

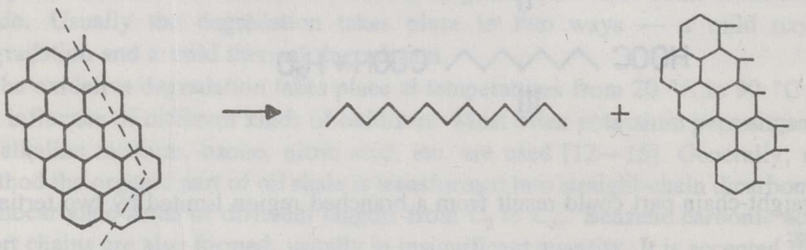
4. There is one more discrepancy between the oxidation results. It could not be explained how e.g. from kerogen of an atomic ratio H/C = 1.35 products with a

ratio approximately 2 (indicating fatty acids) could result, or, in other words, how a structure containing 65 % of =CH-groups and 35 % of -CH_2-groups in average can give a structure built of almost 100 % of -CH_2-groups. This can occur only if an assumption is made that during oxidation =CH-groups are mainly removed from the system, if, for instance, branching points or condensed cycles contain =CH-groups. But in such a case the number of the latter structures has to be significant and the quantity of the straight-chain regions has to be small, respectively. It follows that the interpretation of the results based on carbonic acids obtained hardly could lead to reliable conclusions about the initial structure.

5. It has been pointed out that no matter what the aromatic compound structure is, e.g. xylenes, methylnaphthalenes, anthracene, pyrene, the oxidation always results in a mixture of monobenzenecarbonic acid derivatives [10]. Thus, using this method accurate quantitative results for the number of aromatic carbon atoms or groups of similar structures in the starting kerogen could not be obtained.

6. Structures where the other heteroelements of kerogen — nitrogen and sulphur (except oxygen) — are presented cannot be distinguished and determined by this method.

7. As it is pointed out in [16, 17] one must bear in mind that at thermal degradation straight-chain regions can be formed also at rupturing ("unzipping") of a condensed cyclic structure. It means that similar mechanism could also occur at forming straight-chain dicarbonic acids from a cyclic structure:



(3)

8. An oxygen balance of the direct chemical reaction cannot be made.

9. At industrial production of straight-chain fatty acids by the oxidation of petroleum paraffins always a mixture of mono- and dicarbonic acids of a different length is obtained. The presence of other oxygen-containing groups is observed in some cases, too. This fact evokes a certain doubt about the postulates accepted for interpreting the kerogen structure based on mono- and dicarbonic acids at the oxidation.

10. Interpreting the results of oxidative degradation it is not considered that in that case also an opposite effect could appear: oxidative condensation of non-condensed and low-molecular starting fragments at oxidative polymerization and cyclization, especially at higher temperatures. Such a process is observed, for example, when treating heavy petroleum residues to bitumes.

The other method for studying the kerogen structure is mild thermal pyrolysis in an inert medium, in water steam or in a medium of its own gases. It was successfully applied so far both for kerogen structure examination [3—6, 10, 16—19] and for examination of high boiling hydrocarbon residues of a complex heterostructure [20—22]. It is based on the assumption that under mild thermal conditions fragments separate from the kerogen microstructure. Their examination gives a more realistic idea of the structure they are resulting from. As known from theoretical chemistry, according to the so-called rule for the smallest molecular deformation under mild thermal degradation the molecule degrades in direction requiring the smallest molecule deformation, the structure of the thermal degradation products remaining possibly closest to the starting compounds [23]. It is also proved by the fact that a great quantity of cyclic oxygen-containing structures, aliphatic chains with oxygen functional groups (e.g. ketones), cyclohexanes, alkenes and dialkenes, conjugated dienes, alkane chains, etc. is found among the products of oil shale thermal degradation. Their detailed analyze could more precisely reproduce the initial microstructure. Besides, this method gives an opportunity to establish the complete material balance of the products arising at degradation of the initial structure. The quantities of water, CO_2, and CO enable to make precise conclusions about oxygen-containing groups available in the kerogen structure and to give a picture of the processes. By this method, of course, a great part of oxygen-containing compounds, is also degraded as hydrocarbon structures do. Moreover, surely there occur some secondary processes as well as rearrangement and condensation that would partly change the character of the detached fragments and compounds. For that reason, the mayor efforts at using this method for kerogen structure examination lie in carrying out a mild and fast thermal degradation in an inert medium, in fast evacuating and cooling of the products and also in stopping the oxygen access to them.

A great number of concepts on kerogen structure of various oil shales is collected so far basing on the results of the methods pointed above. Depending on the oil shale types and mostly on the value of the atomic ratio H/C, the concepts on their structures change from one with ordered aliphatic low-network structures up to complete network and highly cyclic structures with a fixed number of aromatic rings [16, 24]. As for the structure of oil shales with H/C from 1.2 to 1.6 we can accept a concise concept according to which their hydrocarbons consist mainly of cyclanic structures of different condensation degrees. The presence of aromatic structures in degradation oil is accepted to be a result of a secondary process of hydrogen redistribution or dehydrogenization of the cycles. No data and suppositions are available about the location and role of the heteroelements. One must consider also that concerning the chemical composition of the organic matter oil shales are more varied than brown and black coals. It is proved that the composition of oil and gas obtained at oil shale thermal degradation well express the initial chemical composition and the structure of kerogen [16, 18].

The chemical composition and structure of Bulgarian oil shales (H/C = 1.3—1.4) have recently been under study mainly by means of oxidation methods [25—28]. Based on these investigations, conclusions have been made that their organic matter is built of polyethylene chains and of insignificant quantity of branched aliphatic chains and aromatic structures [27]. More recent examinations including also the results of thermal degradation have shown that a part of the macrostructure is of a pronounced aromatic character whereby the larger part of the structure is built of partially cyclicized aliphatic groupings [28]. A great part of the organic matter is presented as straight-chain hydrocarbon regions of a length up to C_{33} serving for linking and netting. The degree of branching is low. A certain quantity of aromatic compounds was found in the extracted bitumes [29].

It is evident that there exists some discrepancy in the cited concepts. This provoked us to carry out new investigations for collecting additional data. After comparing the two methods pointed above and the results obtained on their basis we considered the method of mild thermal degradation more suitable for elucidating the kerogen structure of Bulgarian oil shales.

We used this method to determine, relying on the results of the complete analyses of degradation products, the precise material balances of the single groups of compounds and products resulting from the kerogen degradation. The ratio of the numbers of atoms for the different chemical elements per fragment of the kerogen structure has been calculated. This gave us a possibility to draw definite conclusions about the structure of Bulgarian oil shale kerogen and to compare it with its other proposed structures and other types of oil shales.

Experimental

Following the aim of investigations a mild thermal degradation of an exactly defined quantity of oil shale samples was carried out. Parallel to this a great number of their degradation tests was made to characterize the conditions of the process that enabled us to establish the difference in the behaviour of the initial oil shales and the demineralized example during heating; some material balances were examined, too.

A mean sample of Bulgarian oil shale with the following characteristics was used in the investigations, %:

ash A^d	83.6
carbonate $(CO_2)^d_M$	6.1
organic matter (OM) calculated by difference	10.3

The elemental composition of the organic matter on dry ash-free material basis, %:

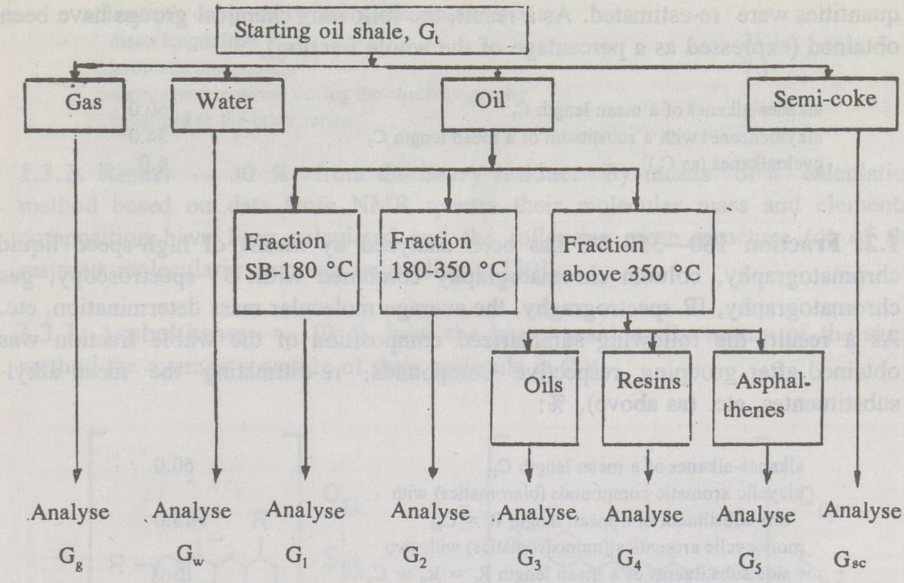
carbon C	76.2
hydrogen H	8.6
sulfur S	0.5
nitrogen N	0.5
oxygen O (by difference)	14.2

Hence, atomic ratios H/C = 1.35 and C/O = 7.15 have been estimated. An oil shale sample of precise weight ground < 0.2 mm was placed in a modified Fischer's retort that was heated at a definite speed (3—5 °C/min), first in a nitrogen medium then in a medium of its own gases. The system was kept under light vacuum aiming at a faster evacuating and cooling of the removed steam-gas mixture.

The following material balance in regard to OM was determined, in wt %:

thermal degradation oil (Schwelöl)	38.8
reaction water	10.7
gas	19.4
semi-coke	31.1

Figure shows the scheme of separating and examining the products of oil shale thermal degradation as well as the way of calculating material balances. Each one of the pointed products has been analyzed in detail as described later. 100 g of organic matter and 10.3 g of oil served as the basis of following estimations.



$$G_t = G_g + G_w + G_o + G_{sc}$$

where

G_t - starting oil shale sample, g
G_g - evolved gas, g
G_w - water, g
$G_o = G_1 + G_2 + G_3 + G_4 + G_5$ - oil, g
G_{sc} - semi-coke, g

A scheme of separation, calculation of the material balances and analyses of the single products obtained at oil shale thermal degradation

1. Analysis of the Obtained Oil

A fixed quantity of the liquid product obtained at the degradation - the degradation oil - was distilled under deep vacuum in an inert medium into three fractions, %:

From the start of boiling (SB) up to 180 °C	21.0
From 180 °C to 350 °C	46.5
A residue boiling above 350 °C	32.5

1.1. Fraction SB — 180 °C has been completely analyzed by means of a capillary gas chromatography under conditions given in [30]. Using this method, 117 compounds in its composition have been identified and quantitatively determined. For our further study they were combined in major groups of compounds. For a given group, they were respectively averaged by molecular mass and their quantities were re-estimated. As a result, the following chemical groups have been obtained (expressed as a percentage of the whole fraction), %:

alkanes-alkenes of a mean length C_8	60.0
alkylbenzenes with a substituent of a mean length C_3	34.0
cycloalkanes (as C_6)	6.0

1.2. Fraction 180—350 °C has been analyzed by means of high-speed liquid chromatography, column chromatography combined with UV-spectroscopy, gas chromatography, IR spectrograghy, the average molecular mass determination, etc. As a result, the following summarized composition of the whole fraction was obtained after grouping respective compounds, re-estimating the mean alkyl-substituentes, etc. (as above), %:

alkanes-alkenes of a mean length C_{17}	60.0
bicyclic aromatic compounds (biaromatics) with one substituent of a mean length $R = C_{10}$	15.0
monocyclic aromatics (monoaromatics) with two side substituents of a mean length $R_1 = R_2 = C_8$	15.0
monoaromatics with one side substituent of a mean length $R = C_{18}$	5.0
monoaromatics with one side substituent of a mean length $R = C_3$	5.0

It has to be noted that during oil distillation, some "dilution" of the distilled compounds took place, as they could not completely be separated according to boiling temperature, and some groups of compounds are found both in the main and some other fraction. This has been considered at their analyses.

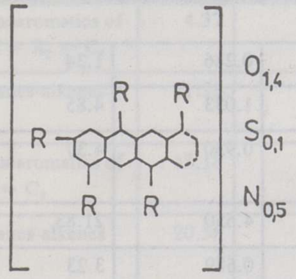
1.3. Heavy residue boiling above 350 °C. Analyzing this fraction was most difficult as it represents a mixture of high-molecular compounds with various functional groups of different reactivity. We have made an attempt to separate this residue by means of corresponding methods into three groups - oils, resins, asphaltenes. These groups have been individually studied by means of several methods: high-efficiency liquid chromatography combined with IR- and UV-spectroscopies, gel permeation chromatography combined with IR-spectroscopy, gas chromatography, pyrolysis chromatography, ^{1}NMR, determination of molecular mass and elemental composition of the groups of compounds. In this way a complete characterization of the heavy residue has been obtained [20]. It could be summarized as follows:

1.3.1. Oils — 60 % from the heavy residue. As above, the single compounds and groups have been respectively summarized, their average composition being re-estimated. The oils consist of the following groups of compounds, %:

n-alkanes C_{17}—C_{32}, quantitatively reduced to a mean length C_{23}	45.9
monoaromatics with one side substituent of a mean length $R = C_{18}$	8.9
biaromatic compounds with one side substituent of a mean length $R = C_{10}$	31.1
triaromatic compounds	7.1
resinous part removed during the chromatography equalized to the other resins	9.1

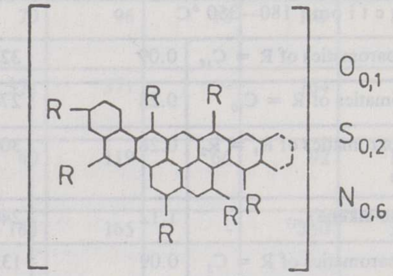
1.3.2. Resins — 30 % from the heavy residue. By means of a calculation method based on data from NMR spectra their molecular mass and elemental composition have been calculated and the following mean structure (4) of the resinous molecule is proposed (according to [30]):

1.3.3. Asphalthenes — 10 % from the heavy residue. By means of the same method the average structure of their molecule is (5):



$R = C_3H_7$

(4)



$R = C_2H_2$

(5)

All quantities of the separate groups of compounds of the oil from initial oil shale thermal degradation thus determined are listed in Table 1. Knowing their quantities and the mean molecular mass, gram-moles of each of the groups in the oil (given in the same Table) could be calculated. For being able to compare the mole parts of all single groups of compounds and products from thermal degradation (i.e. their mole ratios) we assume the following:

— the kerogen macrostructure is significantly homogenous in its whole volume;

— one mean asphalthene molecule has been derived from a studied fragment of the kerogen structure during its thermal degradation.

Other authors also assume that the asphalthenes could be a fragment of the starting kerogen structure [16].

These assumptions open a possibility to determine, with the help of a respective calculating, the mole quantities of all groups of compounds in relation to one asphalthene molecule obtained from one fragment of the kerogen structure at its thermal degradation as well as the atom numbers of this fragment. Following the

Table 1. **Quantitative Composition of the Degradation Oil and Mole Ratio of the Single Groups of Compounds Calculated to 1 Mole of Asphalthenes**

Group of compounds	Quantity, g	Average molecular mass	Number of gram- moles ($\cdot 10^{-3}$)	Number of gram-moles per mole of asphalthenes
Fraction above 350 °C				
Asphalthenes	0.13	610	0.213	1
Resins	0.41	430	0.955	4.49
Oils, including				
- triaromatics	0.11	210	0.524	2.45
- biaromatics of $R_1 = R_2 = C_{10}$	0.24	400	0.606	2.85
monoaromatics of $R = C_{18}$	0.07	325	0.212	1.00
alkanes C_{23}	0.34	325	1.052	4.94
Fraction 180—350 °C				
monoaromatics of $R = C_{18}$	0.09	325	0.286	1.34
biaromatics of $R = C_{10}$	0.28	270	1.033	4.85
monoaromatics of $R_1 = R_2 = C_8$	0.28	300	0.930	4.37
alkane-alkene C_{17}	1.12	240	4.650	21.83
monoaromatics of $R = C_3$	0.09	135	0.689	3.23
Fraction SB—180 °C				
monoaromatics of $R = C_3$	0.29	135	2.12	9.95
alkanes-alkenes C_8	0.50	115	4.38	20.56
cycloalkanes (as C_6)	0.05	90	0.56	2.63

non-complex calculation the results of which are given in Table 1 it is obvious that at degrading of one structural fragment 4.5 moles of resins, 2.5 moles of tricyclic aromatic compounds, 2.8 moles of bicyclic aromatic compounds with two side substituents of a mean length C_{10}, etc., separate together with 1 mole of asphalthenes.

Table 2 gives the atom numbers building the respective mole quantities of the individual groups of compounds based on data in Table 1. These data make it possible to determine the carbon and hydrogen atoms — both of aromatic and aliphatic structures — separately. The coefficient obtained in reducing the asphalthenes to 1 mole (4695) has been used for re-estimation not only in case of oils but also for the other products of kerogen thermal degradation — gas, water, and semicoke.

Table 2. **Atom Number in the Groups of Compounds in Thermal Degradation Oils Calculated to One Mole of Asphalthenes**

Group of compounds	Number of gram-mole	Number of C_{ar}	Number of C_{al}	Total number of C_{at}	Number of H_{ar}	Number of H_{al}	Total number of H_{al}
Asphalthenes	1	32	13	45	25	26	51
Resins	4.49	77	58	135	54	105	159
Triaromatics	2.45	34	5	39	29	15	44
Biaromatics of $R_1 = R_2 = C_{10}$	2.85	40	57	97	23	120	143
Monoaromatics of $R = C_{18}$	2.34	14	42	56	12	87	99
Alkanes C_{23}	4.94	-	114	114	-	237	237
Biaromatics of $R = C_{10}$	4.85	68	49	117	44	102	146
Monoaromatics of $R_1 = R_2 = C_8$	4.37	26	70	96	18	149	167
Alkanes-alkenes C_{17}	21.83	-	371	371	-	764	764
Monoaromatics of $R = C_3$	13.18	79	40	119	66	92	158
Alkanes-alkenes C_8	20.56	-	165	165	-	350	350
Cycloalkanes (as C_6)	0.56	-	16	16	-	16	16
TOTAL		370	1,000	1,370	271	2,063	2,334

Notes: 1. The quantities of the equal groups of compounds from Table 1 are summarized.
2. The indexes "ar" and "al" represent the aromatics and aliphatics, respectively.
3. In the table the oxygen atoms are not shown as their number in resins and asphalthenes is too low. It is presented in the following tables.

2. Gas Analysis

The gas evolved at oil shale thermal degradation has been completely analyzed by means of gas chromatography. The results are presented in Table 3. The volume and weight composition of the gas are also given in Table 3, and the quantities of the compounds obtained during degradation of the kerogen fragment assumed to give one molecule of asphalthene are calculated. From these data the quantities of atoms building them can also be calculated (shown in Table 4). One can see that the number of the hydrogen atoms is about 200 while there are 800 atoms of other compounds. The quantity of methane by mole number is close to that of hydrogen. The mole quantity of CO_2 is several times greater than that of CO (98 against 26, respectively).

Table 3. **Composition of Gas Evolving during Thermal Degradation of a Kerogen Fragment and Number of Moles of the Isolated Compounds**

Compound	Quantity		Quantity, g	Number of gram-moles in gas ($\cdot 10^{-3}$)	Number of gram-moles per 1 mole of asphalthenes
	vol %	wt %			
Hydrogen	25.2	2.1	0.04	21	99
Carbon oxide	7.0	7.9	0.16	6.0	26
Carbon dioxide	25.5	45.7	0.91	21.0	98
Methane	22.6	14.7	0.29	18.0	85
Ethane	6.8	8.4	0.17	5.6	26
Ethylene	4.8	5.5	0.11	3.9	18
Prapane	3.1	5.7	0.11	2.6	12
Propylene	2.9	5.1	0.10	2.4	11
Butanes	1.1	2.7	0.05	0.9	4
Butenes	1.0	2.3	0.05	0.8	4

Table 4. **Atom Balance of Gaseous Products Formed during Thermal Degradation of a Kerogen Fragment**

Compound	Number of atoms in the evolved gas		
	Carbon	Hydrogen	Oxygen
Hydrogen	—	198	—
Carbon oxide	26	—	26
Carbon dioxide	98	—	196
Methane	85	340	—
Ethane	52	156	—
Ethylene	36	72	—
Propane	36	96	—
Propylene	33	66	—
Butanes	16	40	—
Butenes	16	32	—
TOTAL	398	1000	222

3. Water Analysis

The analysis shows that water contains some quantity of phenols and low fatty acids. They are not considered in the next estimations.

The quantity of water separating during the degradation of kerogen fragment is 287 moles on a mole of asphalthenes (obtained by multiplying the quantity of moles of reaction water formed during the degradation by the factor used for oils). The result is 574 hydrogen atoms and 287 oxygen atoms, respectively. Comparing the oxygen atom number separating with the gas it becomes evident that the number of oxygen atoms of the hydroxyl groups nearly 1.3 times exceeds the oxygen present in the removed CO and CO_2.

4. Semi-coke Analysis

Semi-coke contains no soot particles. Moreover, its X-ray analysis permits to conclude that an ordered structure of graphite-like type begins to form.

The elemental composition of the semi-coke resulted from the kerogen of oil shales on dry ash-free material basis, %:

carbon C	93.2
cydrogen H	3.9
sulfur S	0.9
nitrogen N	0.6
oxygen O	1.4

As we know the quantity of semi-coke from the degradation of the assumed fragment giving a mole of asphalthenes, we can determine using the respective coefficient that the structure of the resulted semi-coke is built of 1,167 carbon, 586 hydrogen and 15 oxygen atoms. The elemental composition of semi-coke shown above indicates a presence of some more volatile components that could be separated at heating, mostly in the form of gas containing hydrogen and methane. Accepting

Table 5. **Elemental Balance of Thermal Degradation Products from a Kerogen Fragment**

Product	C_{ar}	C_{al}	C_t	H_{ar}	H_{al}	H_t	O_t	Content, %		
								C_{at}	H_{at}	O_{at}
Oil	370	1,000	1,370	271	2,063	2,334	6	46.7	51.9	1.1
Gas	-	398	398	-	1000	1,000	222	13.6	22.3	41.9
Semi-coke	1,167	-	1,167	586	-	586	15	39.8	13.0	2.8
Water	-	-	-	-	574	574	287	-	12.8	54.2
TOTAL	1,537	1,398	2,935	857	3,637	4,494	530	100.0	100.0	100.0

Note: ar - aromatic; al - aliphatic; t - total that at least half of the available hydrogen separates in the form of methane (this assumption is made with reservations) then nearly 70 carbon atoms will be needed for it — i.e. further heating of the semi-coke will not cause a remarkable change in the carbon number needed for the structure of semi-coke of a graphite-like type.

Before analyzing the data given in the tables, the complete material balance of single atoms from degraded fragment has to be done. A summarized elemental balance for individual products of degradation of a fragment giving a mole of asphalthenes is presented in Table 5. Basing on our results the respective atomic ratios and elemental composition could be estimated to compare with the initial ones. As it is seen from Table 5, about 40 % of carbon builds the semi-coke structure. However, this fact has not been considered in previous discussions of kerogen structure. The atomic ratios calculated by us are H/C = 1.53 and C/O = 5.5. The estimated elemental composition is as following (%): carbon — 73.1; hydrogen — 9.3; oxygen — 17.6 (nitrogen and sulphur summarily amounting to 1 % have not been accounted).

The values of aromatic ratios and the elemental composition calculated on the basis of the elemental balance in the examined fragment show that the quantities estimated for hydrogen and oxygen are higher than their quantities in the initial organic substance. Such discrepancy in balance calculations of similar kind cannot be excluded especially considering the great number of material balances, roundings in estimation of the quantity and the number of the single structures and atoms in them and the possible errors made at various analyses. The larger part of the overestimated hydrogen quantity is found in the oil. One of the reasons is that the hydrogen quantity that could be obtained at forming the unsaturated structures has not been considered — a trial to make it is given further in the text. Probably the increased oxygen quantity is a result of unprecise determination of the removed water, of gas analysis or of the fact that oxygen is estimated usually not directly but by a difference (100 % minus the sum of the rest of available elements). We draw the attention to the inexactness as an overestimated hydrogen quantity. If it would be reduced to the quantity in the initial kerogen then in the oil the alkane-alkene part would be still less due to increasing the part of aromatic structures. In spite of these considerations, we assume that the calculated balance of the single atom distribution has an accuracy allowing conclusions on the fragment structure to be made.

Discussion

A degradation product — semi-coke — has not been taken into consideration at elucidating kerogen structure. However, about 40 % of carbon remains in it. The effect of heteroelements has not been discussed either. Thus these aspects need a special discussion.

Without entering into details of the mechanism for semi-coke production we accept the mayor points of low-temperature carbonization theory. According to the latter, the semi-coke structure seems to be like a starting-point to graphite-like order — a presence of wide regions built of condensed aromatic nets. At a further thermal treating they undergo a spacial rearrangement to a graphite-like structure. As it was pointed out above, the X-ray examinations of semi-coke show elements of a primary graphite-like order. Under the conditions of shale oil thermal degradation — at temperature up to 520 °C, a fast evacuation of the products, absence of catalysts, and slightly reduced pressure — it is less probable that aromatic structures could be formed from aliphatic ones. So, we assume that semi-coke has a structure practically consisting of aromatic nets, and that they have been formed at condensation of aromatic structures available in the kerogen and/or at last, from nets made up of not large cyclic structures undergoing a dehydrogenization process to aromatic structures with the further condensation (dehydropolycondensation). This process (the coking in general) is accompanied by an increased removal of hydrogen and methane. As we already have calculated the balance for hydrogen and methane, we could make some estimations and comparisons for checking this claim.

At kerogen thermal degradation, hydrogen could separate by the following processes: (a) alkene formation; (b) cyclization of alkenes and dialkenes accompanied by dehydrogenization as well; (c) dehydrogenization of available cyclic structures; (d) polycondensation of aromatic structures.

Later on we shall draw the attention to the process of hydrogen rearrangement during kerogen degradation.

(a) The bromine number of liquid products is considered to be a quantitative indicator for alkenes in the liquid product, and the maleinic number shows the quantity of conjugated dienes. Usually they are determined for the benzine fraction only. In our studies we estimated these values for all fractions of oil. Knowing the molecular mass of the studied product and its bromine number, the number of the double bonds in it could be calculated and hence, the quantity of hydrogen separating at alkene production during kerogen degradation can be determined as well. Bromine number 61 g Br_2/100 g oil has been obtained for the thermal degradation oil [20] (100 g Br_2/100 g oil and maleinic number 80 mg/g have been obtained for the benzine fraction). The estimations made for the given structure fragment showed the number of the double bonds to be about 70, i.e. producing alkenes, at least 70 moles of hydrogen have separated. One has to bear in mind that this value could actually be considerably lower than the calculated one, as unsaturated structures could result from the rupture of longer-chain alkanes to shorter-chain alkanes and alkenes as well. The maleinic number shows that hydrogen separation has occurred. In this case the value of maleinic number is not of any importance because it is included in the value of bromine number. But it shows the occurrence of dienes in the oil. Under the conditions of kerogen thermal degradation dienes could form at rupturing of cycloalkanes, too. In that case the maleinic number could be considered an indirect proof for the presence of cycloalkane structures.

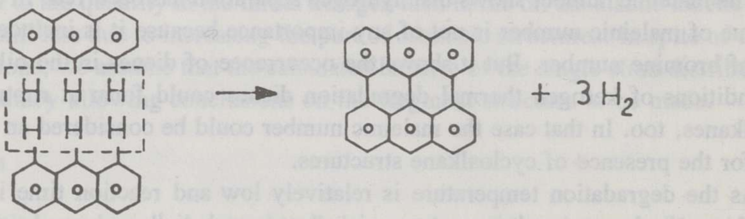
(b) As the degradation temperature is relatively low and reaction time is short, probably no hydrogen evolving occurs via alkenes and dialkenes condensating to aromatic compounds.

(c) The dehydrogenization of cycloalkane cycles is quite possible and probably it is one source for hydrogen getting into the gas. Such an assertion is supported by the behaviour of cycloalkanes at heating — it is directed mainly to the cycle dehydration before the following rupture. The hydrogen quantity that could separate for production of aromatic structures from cyclic ones could be approximately calculated using the data from Table 2. The results are shown in Table 6. One can see that hydrogen quantity, that could separate at aromatizing cyclic structures in oil (provided there are no aromatic structures in the fragment) is about 170 moles. If the aromatic structures would form from aliphatic ones then the hydrogen quantity needed would be still larger.

Table 6. **Number of Hydrogen Atoms Evolved at the Formation of Aromatic Structures from Cycloalkanes Occurring in the Oil Obtained from one Kerogen Fragment**

Group of aromatic structures	Number of moles	Number of cycles per mole	Number of H-moles for producing a mole of aromatic rings in the structure	H-atoms evolved at aromatization of cyclic structures
Asphalthenes	1	8.5	16	16
Resins	4.49	3.5	8	35.9
Triaromatics	2.45	3	7	17.1
Diaromatics + + 2 • R = C_{10}	2.85	2	5	14.3
Diaromatics + + 1 • R = C_{10}	4.85	2	5	24.2
Monoaromatics + + 1 • R = C_{18}	2.34	1	3	7.0
Monoaromatics + + 2 • R = C_8	4.37	3	3	13.1
Monoaromatics + + 1 • R = C_3	1	3	3	39.5
TOTAL				167

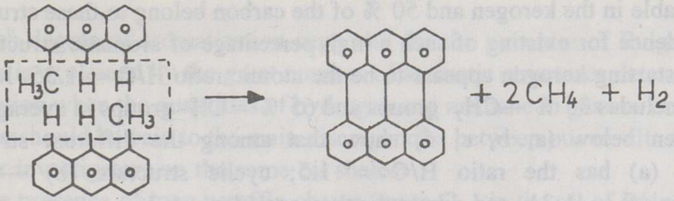
(d) The hydrogen separation during polycondensation of aromatic structures is demonstrated by the following example:



(6)

For the further discussion we assume provisionally that the resin structures are the basic initial constructing elements in semi-coke production. This has been demonstrated by our previous investigations on electrode coke production from an oil residue above 350 °C after oil shale thermal degradation [21, 22]. Besides, the resins have H/C = 1.23 — a ratio close to that of the initial kerogen. The low-nuclear aromatic compounds also condensate to semi-coke but only under a pressure as their larger part distils into the liquid product due to the lower boiling point. We do not suppose asphalthene structures to prevail in kerogen also due to limitations by the atomic ratio (H/C = 0.93). In such case, the semi-coke from the examined structure fragment could be obtained at condensing about 40 cyclic (tricyclic) molecular structures (considering the carbon number in the semi-coke from the fragment). Then, according to the reaction (7) at least 60 more moles of hydrogen would evolve in the gas. At that, we do not take into consideration that at further condensing of the structures obtained by (6), hydrogen evolves, too. Moreover, for the production of these aromatic tricyclic structures from nonaromatic ones, if they did not occur in the initial fragment, about 280 more moles of hydrogen (40 • 7) would separate. The figures do not change when instead of resin structures we consider an equivalent quantity of asphalthene ones.

We draw the attention to the fact that hydrogen separates not only at condensing aromatic structures. It could occur also when short-chain substituents detach themselves according to the reaction and its versions:



(7)

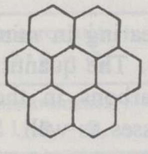
Though this process probably occurs it is not dominating bearing in mind the quantity of methane separating in the gas (altogether 85 moles). The quantities of ethylene and ethane could be added. However, the hydrocarbons in the gas (including methane) are formed during other degradation processes as well. So an equation could be given for the minimum quantity of hydrogen that separates in the gas provided that the aromatic structures are formed during thermal degradation from cyclic structures in the kerogen fragment (including also the hydrogen resulting from the formation of alkenes — 30 moles of hydrogen):

$$280 + 170 + 70 + 60 + 30 = 610 \text{ moles of hydrogen.}$$

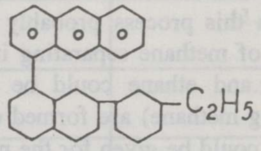
Thus, if no aromatic structures are available in the initial structure of the studied fragment, and they are formed at the degradation, the gas evolved should contain at least 610 moles of hydrogen. If there are aromatic structures in this fragment (identified in the oil and those forming the semi-coke) the corresponding number of hydrogen moles in gas should be 160. According to Table 4, thermal degradation of the fragment leads to the separation of about 100 moles of hydrogen, i.e. a value closer to the needed one especially bearing in mind that hydrogen may separate due to rearrangement reactions, too, this quantity being actually lower than 70 moles. So, the results obtained from these estimations enable us to suppose that very possibly the mayor part of the aromatic structures in the degradation products from the examined structure fragment has not resulted from the thermal degradation including also the semi-coke forming but has been available in the starting kerogen. In such case, according to the data given in Table 5 the basic conclusion is that at least 50 % of the carbon building the structure of kerogen fragment are presented as aromatic structures. The availability of aromatic structures in kerogen explains the discrepancy between the results of kerogen oxidation given in clause 4 and the theoretical values.

Also other processes of rearrangement are possible — e.g. rupturing of larger condensed cyclic structures results in formation of higher aromatized parts and low-molecular straight-chain and/or smaller cyclic structures. However, this does not change our line of reasoning. A comparison of data for the obtained oil shows that a high aromatization could hardly be ensured by the hydrogen rearrangement processes without its separation. For example, according to Table 1, there areal together about 50 moles of alkanes-alkenes separated that should lead to formation of maximum about 50 double bonds. For formation of aromatic compounds available in the oil about 170 moles are needed (Table 6). Adding to them the quantity required for the formation of semi-coke structure it becomes clear that the processes of hydrogen rearrangement during the degradation of the examined kerogen unit could not affect significantly the calculated hydrogen balance and the conclusions made on that basis — i.e. that the major part of the aromatic structures has been available in the kerogen and 50 % of the carbon belong to these structures.

Another evidence for existing of such a high percentage of aromatic structures in the examined starting kerogen appears to be the atomic ratio $H/C = 1.35$. It shows that kerogen includes 35 % $-CH_2-$ groups and 65 % $=CH-$ groups in average. The examples given below (a, b, c, d) show that among the different structures hydrocoronen (a) has the ratio $H/C = 1.5$; cyclic structure (b) — 1.25; alkylanthracene (c) — 1.31, and diheptylanthracene (d) — 1.36.

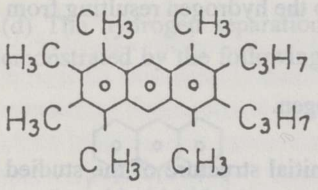


a

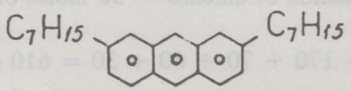


b

(8)



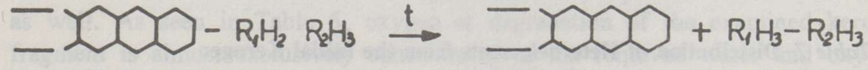
c



d

The last two values are close to H/C of the starting kerogen but only (d) meets the second additional requirement established by our studies, namely $C_{ar}/C_{al} = 1$. The structure (d), however, only formally satisfies both conditions but does not correspond to the products actually produced during thermal degradation. The elaboration of various versions of a cycloaromatic structure including some aliphatic part corresponding to the calculated values of atomic H/C and C_{ar}/C_{al} and being in conformity with the products formed at kerogen degradation gives reason to suppose that in the kerogen there may occur an alternation of condensed regions of the type (d) and of a small quantity of aliphatic portion and cyclic regions of the type (a), the averaging aliphatic portion of the structure (d) probably taking part in intermediate cyclic structure formation — for example, in formation of larger cycles of high oxygen contents. Moreover, other types of inclusions in the whole structure could also take part in the formation of the average value of ratio H/C in the initial kerogen.

We draw a special attention to the process of hydrogen rearrangement between the single structural units and compounds at the kerogen degradation. It has been shown that at the thermal degradation the high-molecular condensation products become poor in hydrogen while the low-molecular compounds become rich in it. This occurs because of the increase in the number of double bonds (without hydrogen separation) according to the reaction:



(9)

The high degree of aromatization supposed for the structure of Bulgarian oil shale kerogen is explained by the great number of aromatic structures determined after its degradation when the quantities of hydrogen and methane in gas are insufficient. But attention should be paid to the main discrepancies between our results and the results of other investigators on the same oil shales:

— The presence of long paraffin chains (up to C_{33}) in the oil of Bulgarian oil shale kerogen thermal degradation [20, 21].

— The results obtained at oxidation of the same oil shale kerogen with $KMnO_4$ according to which about 40 % of the kerogen carbon belongs to structures which are hard to oxidize, specified as "polyfunctional acids" of aliphatic type. Straight-chain dicarbonic acids are obtained mainly when the content of the aromatic carbonic acids is low [25—28].

— The absence of a great number of aromatically linked protons estimated at ^{1}H-NMR spectroscopy of the products.

The first point confirms the supposition made above about the existence of a two-phase kerogen structure. Other types of compounds (except bitumes) are included in the cyclic structures — the long alkane chains mentioned above that could not be extracted due to their strong reactivity concerning other structural units. Their quantity, as could be seen from the compound balance, is not large. Moreover, we agree with the Bandurski's supposition [16] that the formation of a great part of chained structures at a suitable "unzipping" of the cyclic structures at heating is completely possible as it was pointed out in the theoretical part.

Because of practically equal contents of carbon in the semi-coke and in "polyfunctional acids" (PFA) of these oil shales, their low oxidizing ability as well as the constant sum of their low-molecular and high-molecular parts, and continuing oxidation of these acids observed during the examination, it could be assumed that the semi-coke is also formed from PFA during the thermal degradation. Thus the specified "PFA" should be of a completely cyclic type with wide regions of condensed aromatic structures.

The quantity of the aromatic carbonic acids from Bulgarian oil shale oxidation, according to the same studies, coincides approximately with the quantity of mono- and bicyclic aromatic structures determined in the oil of thermal degradation of these oil shales. They are probably located far from the more condensed aromatic part in the kerogen structure and do separate as monoaromatic carbonic acids during oxidation or as mono- and bicyclic aromatic compounds during thermal degradation. As for the discrepancy between the assumption about a significant quantity of aromatic structures in the kerogen and the data on ^{1}H-NMR spectra of its structures, one must bear in mind that when the number of the condensed rings (the degree of condensation) increases the number of the aromatic protons per mole, on one hand, and the aromatic character of the cyclic structure, on the other, correspondingly decrease. This could cause errors in the quantitative determination of these protons. One must also bear in mind that quite a significant part of the high-condensed heterocyclic compounds does not dissolve in the solvents used for taking ^{1}H-NMR spectra that also decreases the accuracy of quantitative determination of aromatic structures.

Table 7. **Distribution of Heteroelements from the Initial Kerogen in its Thermal Degradation Products**

Hetero-elements	Initial kerogen		Gas		Water		Oil		Semi-coke	
	wt%	g	wt%	g	wt%	g	wt%	g	wt%	g
Sulfur	0.5	0.05	abs.	abs.	abs.	abs.	0.5	0.02	0.9	0.03
Nitrogen	0.5	0.05	abs.	abs.	abs.	abs.	0.8	0.03	0.7	0.02
Oxygen	14.2	1.46	37.5	0.75	89.1	0.98	2.4	0.1	1.6	0.05

Note: The oxygen balance as pointed out above is not quite complete. The inaccuracy is due to the fact that oxygen is determined by difference.

Table 8. **Distribution of Heteroelements in the Thermal Degradation Oil and in its Heavy Residue**

Products	Heteroelements					
	Sulphur		Nitrogen		Oxygen	
	% wt	g	% wt	g	% wt	g
Thermal degradation oil	0.50	0.02	0.80	0.03	2.4	0.10
Heavy residue (>350 °C), 32.5 % from the oil	0.50	0.007	0.70	0.009	2.5	0.033
Contents in heavy residue, percentage from the contents in the oil	35		30		33	

Tabel 9. **Participation of Heteroelements in the Structure of Different Fractions of the Heavy Residue, %**

Heteroelements	Asphalthenes	Resins	Oil
Sulphur	14.9	6.5	28.7
Nitrogen	25.3	23.5	2.7
Oxygen	59.8	70.0	68.6

We call the attention of the reader to one more problem less investigated so far. It is the question about the participation of heteroelements — O, S, N — in the kerogen structure. The results of such examinations could also outline their role in the formation of kerogen structure. We begin with oxygen prevailing among the heteroelements.

As it has been mentioned above, phenol content in the obtained oil is low and we have not taken it into consideration; nevertheless, they represent aromatic structures as well. As seen in Table 5, oxygen at degradation of the examined kerogen fragment is almost exclusively concentrated in the removed water and oxygen-containing gases and its quantity in the semi-coke is low. First, we have to point out that the number of oxygen atoms from the fragment removed with reaction water is larger than that removed with the gas. Although the kind of the oxygen compound not always indicates the kind of the structures from what it is formed at rupturing, one may assume that OH-groups prevail and/or there is at least one oxygen atom near two instable hydrogen atoms. The occurrence of enols in kerogen is also not excluded, like it is in case of Estonian oil shales [18]. A strong prevailing of removed CO_2 over CO could not be un-noticed. These gases could not always be obtained quantitatively at rupturing of some structural unit but still it could be assumed that the carbonyl structures are considerably less available than the ester ones. The latter is confirmed also by the absence of carbonyl compounds in the thermal degradation oil (unlike Estonian shale oils).

Further information on the participation of heteroelements in different structures could be gathered on the basis of their distribution in the products of kerogen thermal degradation shown in Table 7.

Table 8 shows the distribution of heteroelements in the degradation oil. From the Tables it becomes evident that oxygen content of kerogen exceeds that of sulphur and nitrogen nearly 30 times. At kerogen degradation oxygen separates mainly in the form of water and gas (CO_2 and CO), and in the other degradation products it is commensurable with the contents of other heteroelements.

Practically, nitrogen and sulphur of kerogen are transferred only into the oil and semi-coke. Nearly 60 % of sulphur and 40 % of nitrogen from the starting kerogen are recovered in the semi-coke structure. This shows the participation of stable cycles of aromatic type. The share of oxygen in such cycles is 3 % of the initial one. Nitrogen compounds of the lighter parts of oil usually being of basic character have been extracted and identified, practically all of them being aromatic compounds. Sulfur compounds of this part of oil have not been examined more closely but basing on other results they might be included in various functional groups.

In the groups — oils, resins, asphalthenes — into which the heavy residue (> 350 °C) is divided oxygen is presented in large amounts (up to 70 % of the total amount of heteroelements in each component) (Table 9). Nitrogen has an equal share in asphalthene and resin structure practically being absent in the oils. Sulphur has the smallest part in resin structure.

Table 10 shows that half of the quantity of sulphur in the heavy residue is concentrated in oils while more than a half of nitrogen and oxygen is present in resins.

Table 10. **Distribution of Heteroelements between the Different Fractions of the Heavy Residue, %**

Heteroelements	Asphalthenes	Resins	Oil
Sulphur	19.0	26.0	55.0
Nitrogen	24.0	71.0	5.0
Oxygen	16.0	57.0	27.0

To get further information, each of the three groups has been subjected to low-temperature carbonization till electrode coke production (up to 520 °C). From the results given in Table 11 it is clear that nitrogen in asphalthenes is present only in condensed cycles of aromatic type. About a half of the sulphur belongs to stable aromatic structure and the other half — in side - probably bridge - bonds of degradable cycles and groups. As for the resins, the larger part of sulphur passes to the semi-coke while nitrogen is found in easier rupturing side structures. In the oils nitrogen is also in the cyclic part, and the larger part of sulphur is found in a degradable non-condensed structure. Under these conditions oxygen separates mainly as water, CO and CO_2.

Table 11. **Distribution of Heteroelements in the Products of Low-Temperature Carbonization of Single Groups of Compounds from the Heavy Residue, %**

Group of Compounds	Sulphur			Nitrogen			Oxygen		
	Coke	Distillate	Gas	Coke	Distillate	Gas	Coke	Distillate	Gas
Asphalthenes	48	52	abs.	100	abs.	abs.	-	Water, CO_2 and CO are produced	
Resins	79	21	abs.	49	51	abs.			
Oils	23	77	abs.	85	15				

Summarizing the results we can assume that during kerogen degradation and low-temperature carbonization practically all nitrogen and the mayor part of sulphur remain in the semi-coke (or coke, respectively) — i.e. they belong mainly to the stable cyclic structure of aromatic type. The share of oxygen in such structures is commensurable with the other heteroatoms. However, taking into consideration its content in the starting kerogen the share of oxygen in aromatic structures is smaller.

We draw the attention to the fact that most of nitrogen and sulphur and some part of oxygen in kerogen are concentrated in stable cyclic-aromatic structures the semi-coke is produced from, as well as in the structure of asphalthenes and resins we consider the central part of a single fragment of the structure. Bearing in mind their great chemical activity (high electronegativity, the presence of free electron couples) we suppose that they serve as reaction centres or take part in the cyclization process along with other processes (e.g. of microbiological type). For that reason, they are mainly included in cyclic structures. Thus heteroelements are found mostly in the resins and asphalthenes and condensed cycles not because they accumulate there but because they have taken part in their formation during the forming of macrostructure. Bearing in mind the great quantity of oxygen and the reactivity of the oxygen-containing functional groups the main role in this respect seems to be played by oxygen. The process of the initial cyclization of large straight-chain structures probably runs with the participation of oxygen-containing functional groups, primary cycles being additionally netted and probably cyclisized and condensed, nitrogen and sulphur-containing groups as well as other active functional groups and/or double bonds naturally taking part in this complex process. At that, as it was pointed out above, the kerogen macrostructure is not built of uniformly alternating aromatic-cycloalkane nuclei but of alternating regions of such kind.

Conclusion

Basing on the presented data and their analysis we could accept the following approximate macrostructure of Bulgarian oil shale kerogen which has probably a two-phase character.

One of the phases is built of two types of alternating regions:

— high-condensed regions of aromatic type with structures similar to those obtained during degradation of asphalthenes and resins;

— regions of condensed cycloalkanes with small cycles with "islets" of mono- and biaromatic alkylated parts between them. The latter could also be bridge-attached to the high-condensed regions of aromatic type.

Between these regions (except in bitumes) there are straight-chain structures, pure alkanes and/or structures containing oxygen in different functional groups (the other phase). Along with them, there are cycles of a great number of carbon atoms that also contain a significant quantity of oxygen-containing functional groups. Part of the dicarbonic acids is obtained during the mild oxidation of kerogen. The semi-coke as well as the resins are produced from the aromatic regions during pyrolysis while the rest of the compounds is produced from the condensed cycloalkane structure and structures of other types located between them. These single parts are tightly bound between the general units of kerogen macrostructure. The results of our investigations (like the coking of coal) show the availability of a weaker bond between separate larger and stabler structures at heating. The great quantity of oxygen and the presence of sulphur and nitrogen that appear to be reactive elements of highly electronegative character with free electron bonds probably have played a significant role in the process of initiating and forming the cyclic and cyclo-aromatic structures in which other active functional groups (and double bonds) and other types of processes (e.g. microbiological ones) have participated.

Based on the developed ideas about the kerogen structure a trial will be presented in the second part of the paper to trace, from the chemical point of view, the possible reactions leading from the supposed initial substances till the formation of kerogen structure.

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Presented by K. Urov
Received May 12, 1993

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