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Abstract

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Electron Paramagnetic Resonance Spectra in Baltic Oil Shales

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The Baltic shale kukersite, in its origin, composition, and properties, occupies a special place among the caustobioliths (1). Present-day views on the chemical nature of kukersite kerogen and on the essence of the transformations occurring during its thermal decomposition are highly contradictory.

The presence in the kerogen of a considerable number of heteroatomic functional groups and the high content of phenols in the products of their thermal decomposition give some investigators grounds for advocating an oxyaromatic structure of the organic matter of kukersite (2,3). Other authors believe that the basis of the kerogen macromolecule consists of closed polymethylene structures, which upon heating are converted into oxyaromatic rings (4). The thermal decomposition of kukersite kerogen, accordingly, is interpreted either as a chain of successive "primary" transformations (5), or is regarded as a complex of successive and parallel primary and secondary reactions (6).

These concepts, formed as a result of indirect chemical-analytical investigations, can be substantially refined and supplemented by studying phenomena that directly characterize the molecular composition and structure of kerogen and the products of its thermal decomposition. In particular, the present article sets forth the results of the first stage in the study of electron paramagnetic resonance (EPR) in the initial and thermally treated oil shale. The main aim of the investigation was to obtain a qualitative characterization of the EPR spectrum in the samples tested.

Objects and Method of Investigation

The first series of samples is represented by three specimens of kukersite from the Kiviõli mine field of the Estonian deposit, with different kerogen contents (concentrate; a mixture of shale from layers A–E of the industrial part of the seam; an unbeneficiated shale from layer A^1 with an increased content of aluminosilicates in the mineral part). For comparison, a sample of dictyonema Estonian shale was also included; its kerogen apparently possesses a condensed aromatic structure and increased thermal stability (1).

The second series of samples is represented by kukersite, crushed to a particle-size class of 3–5 mm (a mixture from layers A–E) and subjected to heating at a constant rate of 13°C per min to a specified temperature (280, 360, 380, 420, 430, 450, 475, and 520°C), followed by isothermal holding for a specified duration. The design of the reactor ensures uniform heating throughout the volume of the fuel layer and a short duration of contact between the volatiles and the solid material, which limits the distorting effect of secondary reactions in the vapor-gas phase (^{7}). Products of benzene extraction of certain samples of thermally treated shale were also studied—the solid residue and the extracted primary bitumen. The characteristics of the samples and the results of the investigation are given in Tables 1 and 2; the composition

the mineral part of unenriched shales, which is not subject to significant fluctuations, has been described in the literature (^{8}).

The EPR spectra were recorded on an instrument assembled according to the usual scheme for recording the derivative of an EPR spectrum, with a sensitivity down to 10^{14} spins, calibrated with DPPH and recorded with an EPP-09 recorder, according to the method described in (^{9}), at 20° and, in some cases, at -196°C with cooling of the ampoule and resonator by liquid nitrogen. The results of the latter measurements will be the subject of a separate communication. Samples of solid material were ground through sieve No. 100; the high-viscosity thermobitumen was dissolved in a twofold amount of benzene.

Table 1

Characteristics and results of investigation of samples of solid material

No.	Material	Mineral-part composition, wt. % A^c	Mineral-part composition, wt. % CO_2^c	Organic matter content, wt. %	Specific resistivity, ohm · cm, alternating current 100 V	Specific resistivity, ohm · cm, direct current 500 V	Relative intensity of EPR signal	Duration of isothermal exposure, min	Molecular weight of resin
	Series 1. Initial shale								

No.	Material	Mineral-part composition, wt. % A^c	Mineral-part composition, wt. % CO_2^c	Organic matter content, wt. %	Specific resistivity, ohm · cm, alternating current 100 V	Specific resistivity, ohm · cm, direct current 500 V	Relative intensity of EPR signal	Duration of isothermal exposure, min	Molecular weight of resin
1	Enriched kukersite	8.73	2.19	89.88	$2.5 \cdot 10^9$	$6.8 \cdot 10^7$	28		
2	Kukersite mixture from layers A—E	46,59	14.96	38.45	$1.68 \cdot 10^{10}$	$2.3 \cdot 10^8$	17		
3	Kukersite from layer A^1	57.65	18.06	24.08	$1.5 \cdot 10^{10}$	$1.8 \cdot 10^8$	10.5		
4	Dictyonema shale	80.35	—	19.65	$4.0 \cdot 10^{10}$	$3.0 \cdot 10^8$	18.5		
	Series 2. A. Thermally treated kukersite from sample 2								

No.	Material	Mineral-part composition, wt. % A^c	Mineral-part composition, wt. % CO_2^c	Organic matter content, wt. %	Specific resistivity, ohm • cm, alternating current 100 V	Specific resistivity, ohm • cm, direct current 500 V	Relative intensity of EPR signal	Duration of isothermal exposure, min	Molecular weight of resin
5	Shale heated to: 280°	48.75	17.21	34.04	$9.8 \cdot 10^{11}$	$5.5 \cdot 10^{10}$	25	120	
6	360°	50.29	19.07	30.64	$3.1 \cdot 10^{11}$	$2.0 \cdot 10^{10}$	42	60	
7	380°	50.57	18.61	30.82	$3.0 \cdot 10^{11}$	$1.6 \cdot 10^{10}$	43.5	30	
8	420°	57.60	19.80	22.54	$3.35 \cdot 10^{11}$	$1.8 \cdot 10^{10}$	136.5	20	
9	430°	57.36	20.09	22.55	–	$5.1 \cdot 10^{10}$	118.0	20	208
10	450°	59.85	20.71	19.44	$6.5 \cdot 10^{11}$	$4.7 \cdot 10^{10}$	99.0	0	
11	450°	61.75	21.99	16.26	$5.3 \cdot 10^{11}$	$4.2 \cdot 10^{10}$	108.0	15	215
12	450°	64.45	23.01	12.54	$4.4 \cdot 10^{11}$	$3.6 \cdot 10^{10}$	162.0	30	221
13	475°	64.95	23.06	11.09	–	$2.6 \cdot 10^{10}$	129.5	0	175
14	475°	66.88	23.45	9.67	–	$2.2 \cdot 10^{10}$	193.0	15	183
15	520°	68.54	23.17	8.29	–	$3.4 \cdot 10^{9}$	207.0	0	224
16	520°	68.79	24.61	6.60	–	$5.3 \cdot 10^{8}$	216.0	15	223

No.	Material	Mineral-part composition, wt. % A^c	Mineral-part composition, wt. % CO_2^c	Organic matter content, wt. %	Specific resistivity, ohm · cm, alternating current 100 V	Specific resistivity, ohm · cm, direct current 500 V	Relative intensity of EPR signal	Duration of isothermal exposure, min	Molecular weight of resin
	B. Solid residue after extraction								
17	Shale residue 360°	50.33	18.15	31.52			48.5		
18	380°	52.16	18.12	29.72			60.0		
19	420°	60.26	19.84	19.90			141.0		

Table 2

Characteristics of thermobitumens

No.	Material	Elemental composition, wt. % C	Elemental composition, wt. % H	Elemental composition, wt. % O + N + S	Molecular weight	Relative intensity of EPR signal	Kerogen yield, wt. %
20	Extract from shale at: 360°	79.65	14.30	6.05	930	3.5	4.1
21	380°	82.66	10.98	6.36	818	5.0	12.4
22	420°	84.74	10.57	4.69	750	34.0	30.5

Figure 1: EPR spectrum of the concentrate (a), dictyonema shale (b), and unenriched combustible shale (c).

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Main results. The EPR spectrum recorded at 20° for the concentrate (Fig. 1, *a*) indicates the presence of a comparatively intense signal with factor $g = 2.002$, half-width $\Delta H = 0.6$ gauss, and a number of unpaired spins $\sim 10^{17}$. Dictyonema shale is also characterized by a narrow but sufficiently intense signal (Fig. 1, *b*), similar to the DPPH spectrum. In this case $g = 2.002$, $\Delta H = 0.6$ gauss.

As is known, polyconjugated and aromatic structures are characterized by a narrow one-component signal with a g-factor equal to the g-factor of the free electron.

The EPR spectrum obtained for the concentrate confirms assumptions regarding the considerable compactness of kukersite kerogen, but does not provide an unambiguous answer to the question of the nature of its structure.

For unenriched shale (samples 2 and 3), as well as for samples 5–16 subjected to heat treatment (Table 1), a seven-component signal with $\Delta H = 55$ gauss was obtained (see Fig. 1, *c*). Enrichment of the shale leads to the removal from it of those systems that give a multicomponent signal, apparently of mineral origin (in all probability, Mn compounds).

The structure of these signals remains unchanged over the entire temperature range studied.

Since the EPR spectra for samples of series 2 were studied mainly only qualitatively, Table 1 gives the results of an approximate comparison of the intensities of the EPR signals, expressed in arbitrary units, and the specific resistance in ohm • cm.

Fig. 1. EPR spectrum of the concentrate (*a*), dictyonema shale (*b*), and unenriched combustible shale (*c*).

With an increase in the temperature of isothermal holding from 280 to 360°, the intensity of the signals for shale held for 120–130 min increases only slightly. A sharp increase in the intensity of the EPR signal corresponds to $t_\text{v} = 420°$. Since the intensity of the EPR signals depends both on the value of t and on the duration of the isothermal holding τ, Fig. 2 presents the curve of the dependence $I = I(t_\text{v})$ at $\tau = \text{const}$.

As is seen from consideration of Fig. 2, the curve of this dependence has two inflection points in the temperature region $\sim 420°$ and $\sim 450°$. This curve well confirms the point of view previously advanced by one of us (^{6}) on the role of secondary reactions in the processes of thermal decomposition of shale. Fig. 2 also presents the curve of the dependence of the specific resistance of the

Fig. 2. Curves of the dependence of the intensity of the EPR signal, expressed in arbitrary units, and of the specific electrical resistivity on the temperature of isothermal holding of shales

Figure 2: Fig. 2. Curves of the dependence of the intensity of the EPR signal, expressed in arbitrary units, and of the specific electrical resistivity on the temperature of isothermal holding of shales

material on the temperature of isothermal holding; it is antipodal to the EPR curve, which usually occurs in a certain temperature interval for polyconjugated systems.

In the EPR spectra for the solid residue after extraction, a picture is observed that is apparently analogous to that described above. However, with an increase of t_{v} from 360 to 380°, the intensity of the signals increases somewhat more markedly than for samples 6 and 7. The intensity of the signals for this group of samples at all values of t_{v} seems to be somewhat higher than for material not subjected to extraction. This means that in the solid residue after the theoretically complete removal of the primary decomposition products distillable under the given conditions, there probably remains the chemically most compacted part of the decomposed kerogen, with which is also associated

the observed EPR spectrum. This portion is the initiator of the formation of the condensed fraction of the heavy tar and of still more compact coke; active coke formation under these conditions apparently begins at 430–440°.

On the basis of Table 1 one can also follow the kinetics of the growth of the EPR-spectrum signal at $t_{\text{v}} = 450^{\circ}$. At $\tau = 0$, $I = 99.0$; at $\tau = 15$ and 30 min, $I = 108$ and 162, respectively.

The data given for the values of I refer to the total solid residue; however, the fraction of the organic part in it decreases with increasing t_{v} and τ, and therefore the actual increase in the intensity of the EPR signals is much more substantial.

The data for the bitumens are given in Table 2.

Fig. 2. Curves of the dependence of the intensity of the EPR signal, expressed in arbitrary units, and of the specific electrical resistivity on the temperature of isothermal holding of shales

The EPR spectra for the extracted mixture of primary products (bitumens) are characterized by a significantly reduced EPR-signal intensity in the low-temperature bitumens in comparison with the total thermally treated material; the intensity of the signals increases on going from $t_{\text{v}} = 360^{\circ}$ to 420°. Nevertheless, a highly characteristic indication of the occurrence of secondary reactions, even at a relatively low temperature and a small degree of decomposition of the kerogen, is the appreciable, but quite obvious, increase in signal intensity in the low-temperature bitumen as the temperature is raised from 360 to 380°.

It should also be noted that the signal intensity for the bitumen dissolved in benzene does not decrease during three days after dissolution.

Comparison of the qualitative data obtained with the results of EPR studies in various coals (10–12) indicates the considerably lower thermal and chemical stability of kukersite kerogen and the active role of secondary condensation and compaction reactions even at a relatively low shale-heating temperature.

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CITED LITERATURE

1. A. F. Dobryanskii, *Goryuchie slantsy SSSR*, 1947.
2. A. Ya. Aarna, E. T. Lippmaa, *Tr. Tallinsk. politekhn. inst.*, A, **3**, No. 63 (1955).
3. S. S. Semenov, *Izv. EstSSR*, No. 9 (1958).
4. A. S. Fomina, *Izv. EstSSR*, No. 4 (1954).
5. A. Ya. Aarna, E. T. Lippmaa, *Tr. Tallinsk. politekhn. inst.*, A, **4**, No. 97 (1957).
6. M. Ya. Gubergrits, *Izv. EstSSR*, No. 4 (1960).
7. M. Ya. Gubergrits, B. K. Brodskaya et al., *Byull. Podzemnaya gazifikatsiya ugley*, No. 4 (1959).
8. B. K. Torgan, *Tr. Tallinsk. politekhn. inst.*, A, **2**, No. 57 (1954).
9. Yu. A. Kolbanovskii, I. M. Kustanovich, L. S. Polak, A. S. Shcherbakova, *DAN*, **129**, No. 1 (1959).
10. D. J. Ingram, *Nature*, **174**, No. 4, 434 (1959).
11. A. A. Galkin, D. A. Kitilin, *Khim. i tekhnol. topliv i masel*, No. 7 (1958).
12. N. S. Garif' yanov et al., *Khim. i tekhnol. topliv i masel*, No. 2 (1957).

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