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ESR SPECTRUM OF THE OXIDIZED VANADYLPORPHYRIN COMPLEX OF KARAZHANBASS PETROLEUM

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As a result of the use of various oxidants, mono- and bications of the natural vanadylporphyrins of Karazhanbass petroleum have been obtained, and their ESR spectra have been studied.

In [1], the electron spin resonance (ESR) spectra of vanadyletioporphyrin (VOEP) and vanadyltetraphenylporphyrin (VOTPP) and their various oxidized forms obtained under the action of Lewis acids and bromine are given.

In order to study the natural vanadylporphyrins (VOPs) present in the petroleum oils of the Caspian oil-bearing regions we have considered the ESR spectra of the complex isolated from Karazhanbass petroleum and the products of its oxidation. The vanadylporphyrin complexes were isolated by the extraction-chromatographic method and were identified from their characteristic absorption bands [2] on a Specord UV-Vis spectrophotometer at room temperature. The purity of the vanadylporphyrins isolated was determined from the absorption band at 408 nm (Soret band) and also on the basis of the absence of background absorption in the 400-600 nm region. The degree of purity of the samples obtained ranged between 80 and 95%. The complexes isolated consisted of a mixture of homologs of the vanadyl derivatives of deoxophylloerythroetioporphyrin (DPEP) and etioporphyrin (EP) [3]. The oxidants used were $SbCl_5$, $TiCl_4$, and Br_2.

The ESR spectra were taken in CH_2Cl_2 solution at 77 and 300 K on a Varian E-12 ESR spectrometer. Figure 1 shows the isotropic spectra at 300 K and Fig. 2 the anisotropic spectra at 77 K of vanadylporphyrin and its oxidized forms obtained under the action of various oxidants. An extract containing the complex VOP was obtained by the extraction-chromatographic method.

Table 1 gives the measured and calculated spectral parameters. The action of oxidants led to a decrease in the isotropic HFS constants (a_V) and in the anisotropic HFS constants A and B, and also to a change in the ratio of $g_\parallel$ and $g_\perp$ (in the initial complex, $g_\parallel < g_\perp$, and in the oxidized complexes $g_\parallel > g_\perp$). The change in the ratio of $g_\parallel$ and $g_\perp$ is reflected in the nature of the broadening of the HFS line in the isotropic spectra [1]. In the initial complex, VOP, the high-field components are broadened, while in the oxidized complex it is the low-field components. The values of $g_\perp$ and B for the oxidized forms were determined from the relations $g_{iso} = 1/3(g_\parallel + 2g_\perp)$ and $a = 1/3(A + 2B)$. A comparison of the results obtained with those given in [1] shows that the action of $SbCl_5$ and $TiCl_4$ apparently leads to the formation of bicationic complexes.

The action of bromine, as a weaker oxidant, probably leads to the formation of a monocation. As can be seen from Fig. 1, d, the spectrum consists of the superposition of the

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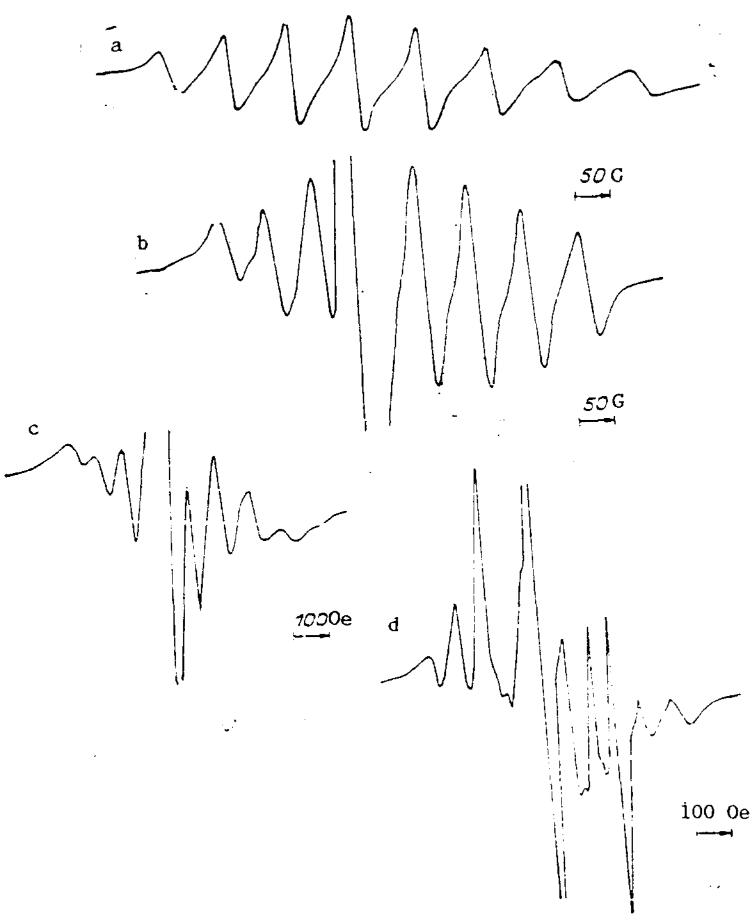

Fig. 1. Isotropic spectra of VOP and its oxidized forms at 300 K in CH_2Cl_2: a) VOP; b) VOP with $TiCl_4$; c) VOP with $SbCl_5$; d) VOP with Br_2.

TABLE 1. Spectral Parameters of Vanadylporphyrin and the Products of Its Oxidation by Lewis Acids and Br_2

Complex	Oxidant	g_{iso}	$g_{\parallel}$	$g_{\perp}$	a, Oe	$A \cdot 10^{-4}$, cm^{-1}	$B \cdot 10^{-4}$, cm^{-1}
VOP	—	1,988	1,956	1,991	92	150	69
VOP^{2+}	$SbCl_5$	1,992	1,988	1,994	80	148	37
VOP^{2+}	$TiCl_4$	1,969	1,975	1,996	72	133	33
VOP^{+}	Br_2	1,985	—	—	47	—	—

spectrum of the initial VOP and the spectrum of the monocation VOP^+. As shown in [1], the ligand undergoes oxidation and the state VO^{2+} is stable in relation to the action of oxidants. A feature of the spectrum of VOP^+ consists in the fact that the value of a_V is half of a_V in the initial complex. This is obviously connected with the exchange interaction of an unpaired electron localized on the vanadium atom and an unpaired electron localized in the ligand. As follows from [4], such exchange must lead to a halving of a_V.

The ESR spectrum of this sample at 77 K differed little from the initial spectrum since only a part of the VOP was oxidized and the spectrum of the biradical proved to be masked by the broader anisotropic spectrum of VOP. According to [1], the spin-spin splitting constant in the monocation is of the order of 0.04 cm^{-1}, which is smaller than the extent of the anisotropic spectrum.

A feature of the spectra of the oxidized forms of VOP is the presence in them of a signal from cation radicals of condensed aromatic compounds. The "carbon radical" usually

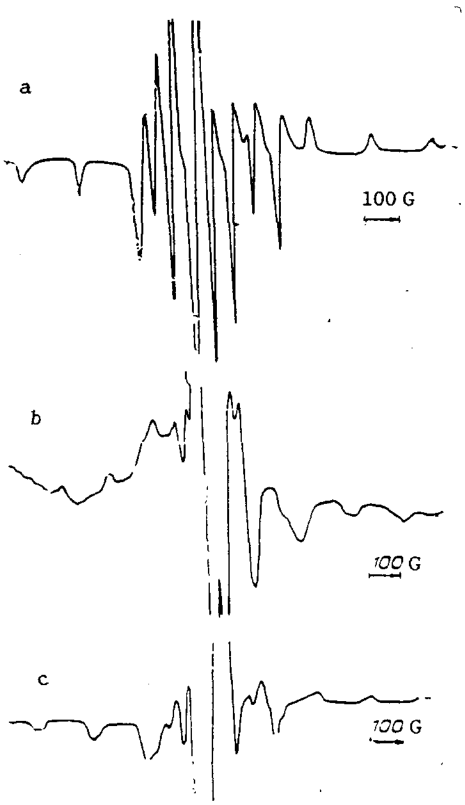

Fig. 2. Anisotropic spectra of VOP and its oxidized forms at 77 K in CH_2Cl_2: a) VOP; b) VOP with $TiCl_4$; c) VOP with $SbCl_5$.

present in the ESR spectra of petroleum oils, relating to high-molecular-mass asphaltenes, was absent from the initial extract (see Figs. 1, a and 2, a). The appearance of a signal of a cation radical is obviously connected with the oxidation of low-molecular-mass condensed aromatic molecules present in the extract. It appears of interest to elucidate the nature of these compounds and their state (whether they are present in a complex with VOP or in the free state).

The different structures of the porphyrins (DPEP and EP) had no appreciable influence on the ESR spectra of the complexes studied.

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