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INVESTIGATION OF THE STRUCTURE OF CARBONIZATION PRODUCTS OF CARBON-CONTAINING SUBSTANCES BY THE METHOD OF ELECTRON PARAMAGNETIC RESONANCE AND BY X-RAY DIFFRACTION

In recent years it has been shown by the method of electron paramagnetic resonance (e.p.r.) that, in the carbonization products of various organic compounds, free radicals are formed whose concentration reaches 10^{19}–10^{20} g^{-1} (1). The e.p.r. absorption method makes it possible to detect free radicals directly in the system under investigation and to determine their concentration; on the basis of an analysis of the shape of the absorption line and its width, conclusions may be drawn about the properties of the free valences and about their interaction with the surrounding atoms.

In order to clarify the possibilities opened up by a joint investigation of the structure of carbonized substances by the e.p.r. method and by X-ray diffraction, we have studied the structural changes occurring during the carbonization of polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC). Carbonization was carried out in an inert atmosphere in the temperature range 350–700°C. The e.p.r. spectra of all samples were recorded in high vacuum on an e.p.r. spectrometer operating at a frequency of 9370 Mc. The signal was recorded on the screen of an oscillograph or on the tape of a recorder in the form of the first derivative of the absorption curve. A thin-walled glass ampoule with the sample, placed in the resonator, was connected to a high-vacuum system, and evacuation of the sample was carried out directly in the resonator. For all the samples investigated, the g-factor (2.0036) was close to the g-factor of the free electron (2.0023). The principal measured parameter was the line width (the distance between the points of maximum slope of the absorption curve).

As is known, in systems consisting of "light atoms" (H, C, O, N), the width of the e.p.r. line from unpaired electrons is determined mainly by dipole interactions of the magnetic moments of the unpaired electrons in the sample with one another and by their interactions with the moments of H or N nuclei. The first type of interaction leads to so-called spin-spin broadening, the second to an increase in the total line width through the appearance of hyperfine structure (h.f.s.) of the e.p.r. line. On the other hand, it is known that, in the presence of a sufficiently strong exchange interaction between unpaired electrons or upon delocalization of the unpaired electrons over a system of conjugated chemical bonds, the local fields caused by the above-mentioned interactions are averaged, which leads to a narrowing of the e.p.r. line and to a change in its shape (transition from Gaussian to Lorentzian ([2])). In the case of systems in which interaction with nuclear moments and exchange interaction occur simultaneously, a decrease in the total line width and a smearing of the hyperfine structure are observed ([3]). Thus, analysis of the width and shape of the e.p.r. line can provide valuable information about the site of localization of the unpaired electrons and about the structure of the substance under investigation.

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Fig. 2. X-ray diffraction patterns of the carbonization products of polyvinyl chloride
(*a*–350°, *b*–450°, *v*–500°, *g*–600°) and polyvinylidene chloride
(*d*–350°, *e*–450°, *zh*–600°, *z*–700°)

To the article by D. M. Chizhikov and A. M. Grinko, p. 278

Fig. 1. A rod of niobium iodide. 6×

The EPR absorption signal, indicating the presence of free radicals, appears at the very first stages of carbonization of PVC and PVDKh (beginning at 350°). Fig. 1 shows the change in the width of the EPR signal (ω) for both substances as a function of the carbonization temperature. For PVC, the line width during carbonization decreases from 7.0 G (350–450°) to 0.8 G (650°). With a further increase in the carbonization temperature, the line begins to broaden (1.2 G at 700°), and upon calcination above 900° such a sharp broadening of the line is observed that observation of the signal becomes very difficult.

The relatively large line width (7 G) in PVC indicates a substantial influence of hyperfine splitting on hydrogen nuclei. Such large widths are characteristic of some natural coals*. In the case of specially prepared coal containing no H atoms (carbonization of C_3O_2), EPR gives a very narrow line (~ 0.6 G), which confirms the view expressed above regarding the broadening of the EPR line in coal due to hyperfine splitting on hydrogen ([5]).

In the case of PVDKh (Figs. 1, 2, 3), especially at the initial stages of carbonization, the EPR line is considerably narrower than for the carbonization products of PVC. Beginning at a temperature of 550°, a second broad EPR absorption signal appears (Figs. 1, 3).

For explaining the features of the EPR curves for PVC and PVDKh, information on the molecular structure of the samples studied, obtained by the X-ray method, was used. X-ray patterns of the carbonization products of PVC (350°) (Fig. 2a) indicate the presence of carbon networks in the sample (from the

Fig. 1. Change in the width of the EPR line of carbonization products of polyvinyl chloride (a) and polyvinylidene chloride (b) as a function of carbonization temperature

Figure 1: Fig. 1. Change in the width of the EPR line of carbonization products of polyvinyl chloride (a) and polyvinylidene chloride (b) as a function of carbonization temperature

presence of the (10) line in the X-ray pattern) and that the networks are separated by irregular structures (from the absence of the (002) line in the X-ray pattern and the presence of a large background in the center of the X-ray pattern). According to generally accepted ideas, free radicals in coals are formed in side chains as a result of the rupture of C—C or C—H bonds (6). Therefore one may expect that, in a structure with very long inter-network chains with slight conjugation, the radicals will be sufficiently removed from the conjugated system of bonds in the carbon networks, and the exchange interaction of the unpaired electron with the conjugated π-bonds of the condensed rings will not be sufficiently strong. In other words, the exchange narrowing of the EPR line, whose width is determined by the hyperfine structure from hydrogen nuclei, will not be very large.

Fig. 1. Change in the width of the EPR line of carbonization products of polyvinyl chloride (*a*) and polyvinylidene chloride (*b*) as a function of carbonization temperature.

From the X-ray data it is seen that raising the calcination temperature to 450° changes little the character of the structure of the carbonization products from PVC (Fig. 2b). The magnitude of the EPR absorption line also remains practically unchanged.

Further carbonization of PVC (500-600°) leads to the appearance in the X-ray patterns of the (002) line, to a decrease in the background inside this ring, which indicates a decrease in the disorder of the structure, and to a narrowing of the (10) line owing to an increase in the size of the networks (Figs. 2v, g). These changes are connected both with the shortening of the side chains and with an increase of conjugation in them. Improvement of the conditions for conjugation of unpaired electrons with the π-bonds of the aromatic rings may also occur as a result of the approach of free radicals to the packets of nets. The facilitation of conjugation conditions leads to exchange interaction and, consequently, to an additional narrowing of the EPR line. In addition, the magnitude of the hyperfine splitting also decreases, since in high-temperature carbonization products the relative hydrogen

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* EPR line widths of the same order were obtained by us for a number of lean natural coals; analogous data are given in work (4).

content is lower.

Calcination of PVC at higher temperatures leads to a considerable increase in the dimensions of the carbon nets and to their mutual ordering. As a result of these changes, conduction electrons appear in the system. The interaction of the unpaired electron with the conduction electrons evidently also leads to the experimentally observed broadening of the EPR line for the PVC sample obtained at a temperature above 700°.

In PVDC, already at 350° there are small nets (see Fig. 2d); the regularity of this structure, judging from the presence of a diffuse ring and the comparatively small background within it, is considerably higher than for the analogous sample from PVC. The smaller width of the EPR absorption line for carbonized PVDC indicates better conjugation of this system in comparison with carbonized PVC.

As already noted, an increase in the carbonization temperature of PVDC above 500° leads to the appearance of a second EPR signal, the width of which increases as the carbonization temperature is raised. It is interesting that, in the case of petroleum cokes calcined at different temperatures, the splitting of the signal coincided with a sharp increase in electrical conductivity. For cokes calcined at comparatively low temperatures (up to 700°), a single narrow EPR signal (2-4 gauss) and very low electrical conductivity ($< 3 \cdot 10^{-4}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$) are observed. At a coke-treatment temperature of about $\sim 800°$, a second broad EPR signal appears (150 gauss), and the electrical conductivity increases to $\sim 10^{-3}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. Raising the temperature to 1100–1300° leads to such a large broadening of the signal that the EPR line is practically not observed, while the electrical conductivity increases to $\sim 2 \cdot 10^{-3}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$.

The presence, at high temperatures, of two EPR signals, in our opinion, indicates the existence in the sample of two types of unpaired electrons, differing evidently in the sites of their localization and in the structure of the surrounding lattice of bonds. It may be supposed that the narrow signal, as in the case of PVC, is due to free valences localized on side chains with strong exchange interaction among themselves through the system of conjugated side bonds. Following the ideas developed above concerning the width of the EPR line in carbonaceous substances, the appearance of the broad signal may be associated with the presence of free valences near individual large carbon nets or packets, in which conduction electrons appear.

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