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INVESTIGATION OF FREE RADICALS FORMED IN SOLIDS DURING IRRADIATION WITH FAST ELECTRONS

In recent years the method of electron paramagnetic resonance (EPR) has found wide application for the study of radicals in various substances subjected to the action of ionizing radiation. However, as far as we know, up to the present time no attempts have been made to study radicals by the EPR method directly during the action of ionizing radiation on a substance. Meanwhile, such a study is of substantial interest, since it is often assumed that the radicals arising under the action of radiation may have short lifetimes and, consequently, can be recorded only during irradiation.

In our laboratory an attempt has been made to detect radicals with short lifetimes in certain solids under the action of fast electrons. In the present work we give data on the study of radicals with lifetimes of the order of several minutes.

An apparatus was assembled that made it possible to record the EPR spectrum directly during irradiation of the sample under investigation. To record the paramagnetic-absorption signal an EPR spectrometer with high-frequency modulation of the magnetic field (1), operating at a frequency of about 9400 Mc/s, was used. The derivative of the absorption signal was recorded on an EPP-09 recorder every 30 sec. The radiation source was a high-voltage accelerator installation giving a beam of electrons with energies up to 2 Mev. The current density at the sample could be varied within the limits 0.03-30 μa/cm^2, which corresponded approximately to dose rates of $6 \cdot 10^3$–$6 \cdot 10^6$ rad per second. The electron beam with an energy of 1.6 Mev was introduced into the region of the magnetic field through a cylindrical channel in one of the pole pieces of the magnet, parallel to the direction of the magnetic-field lines. The diameter of the channel at the exit into the magnet gap was 6 mm. The presence of the channel produced, at the location of the sample, an inhomogeneity of the magnetic field of $\sim$ 0.8 oersted/mm in the direction of the channel axis. The

Fig. 1. E.p.r. signal from polyethylene after switching off the electron beam. *a* —immediately after switching off, *b*—after 1 min., *v*—after 4 min.

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samples studied were made in the form of tablets 5 mm in diameter and about 2 mm thick. They were placed in the resonator at the end of a glass capillary. To measure the temperature, a thermocouple was pressed into the center of the sample. Blowing the sample with a stream of heated or cooled air made it possible to vary the temperature within the range from $+150$ to $-100°$.

Preliminary experiments were carried out at room temperature. The EPR signal was observed during irradiation of the sample and after cessation of irradiation. More than 20 different substances were studied, including polymers (polyethylene, nylon, capron, polymethyl methacrylate, Teflon, and various rubber samples), solid organic acids and their salts (oxalic acid and its salts, succinic acid and its sodium salt, stearic and citric acids), aromatic compounds (naphthalene, α- and β-naphthols, benzoyl peroxide, metol).

In all the samples studied, the radical concentration reached saturation at doses on the order of several tens of megarads. In most substances the radicals obtained proved to be rather stable. Their lifetimes amounted to several hours, and in some cases even more. In naphthalene and in α- and β-naphthols, the signal intensity at comparable irradiation doses proved to be considerably smaller than in the other substances. Radicals with relatively short lifetimes at room temperature were registered in polyethylene, oxalic acid, benzoyl peroxide, and in one of the rubber samples. In the last two substances, several radicals appeared upon irradiation. In both cases, one of the radicals proved less stable than the others. In benzoyl peroxide the unstable radical disappeared within several minutes, while in rubber it was observed only during the irradiation process, i.e., in any case it had a lifetime of less than 30 sec. In oxalic acid, the lifetime of the free radical at room temperature is 2–3 min., which made it possible to study in greater detail the kinetics of its recombination.

Fig. 1. E.p.r. signal from polyethylene after switching off the electron beam. *a*—immediately after switching off, *b*—after 1 min., *v*—after 4 min.

Upon irradiating polyethylene we succeeded in registering the radical

$$-\mathrm{CH_2} - \dot{\mathrm{C}}\mathrm{H} - \mathrm{CH_2}-,$$

which, as is known (^{2}), is unstable at room temperature. The spectrum of this radical is shown in Fig. 1 *a*; it was recorded immediately after the cessation of irradiation, which had lasted several seconds. Spectra *b* and *v* were recorded, respectively, 1 and 4 min. after spectrum *a*.

Spectrum *v* practically does not change its shape with time, i.e., it is produced by a secondary, more stable radical. Spectrum *b* is a superposition of the spectra of the primary and secondary radicals. Comparison of spectra *a*, *b*, and *v* shows that, along with the transition of one radical into another, there is a decrease in the total concentration of radicals. Observations carried out at temperatures below room temperature showed that the rate of transition of the primary radical into the secondary one decreases as the temperature is lowered. Thus, at -18°, over the course of 6 min., there occurred only an insignificant change in the shape of the initial signal, i.e., the secondary radical did not appear in noticeable quantities during this time. Comparison of these results with the data of work (2) shows that the formation of radical *a* is the primary chemical act in the irradiation of polyethylene. Low temperatures prevent its conversion into radical *v*.

In conclusion, it should be noted that significant concentrations of stable radicals in most of the solid substances we studied could hinder the observation of radicals with lifetimes on the order of seconds or less. To isolate the spectra of such radicals we shall use the method of periodic modulation of the electron beam. For the registration of radicals with short lifetimes in solid substances and especially in liquids, it is also proposed to apply a pulsed technique.

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