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Abstract

Full Text

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Migration of Free Valence in Stabilized Olefin Radicals under the Action of Light

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As was shown earlier (^1), under the action of light there occurs a migration of the free valence of radicals formed by γ-irradiation of certain polymers and stabilized at the temperature of liquid nitrogen. The conclusion that such migration exists follows from an analysis of changes in the hyperfine-structure EPR spectra of γ-irradiated polypropylene and other polymers under the action of light. In this process the unpaired electron moves along the macromolecule away from the double bond, and allylic radicals are converted into the energetically less favorable alkyl radicals. After the light is switched off, at the temperature of liquid nitrogen, the reverse process of conversion of the alkyl radical into the allylic one slowly takes place. Thus, these processes are reversible. The question arises whether such reversible transformations of stabilized radicals are characteristic only of polymer macromolecules, or whether this phenomenon is of a more general nature and is inherent in stabilized radicals of various types.

Fig. 1. EPR spectra: *a* —*n*-decene-1, *b* —*n*-octene-2, *v* —*n*-hexene-1 after γ-irradiation at 77° K; *g*, *d*, *e* —the same samples after additional irradiation with light (BS-8 filter) at 77° K from 3 to 5 hours; *zh*, *z*, *i* —after subsequent storage in liquid nitrogen (from three days to 5 months).

To clarify this question we investigated the action of light on radicals formed by γ-irradiation and stabilized at the temperature of liquid nitrogen in certain olefins. *n*-Decene-1, *n*-octene-2, *n*-heptenes, *n*-hexenes, and *n*-pentenes were investigated. Irradiation was carried out with Co^60 γ-radiation at an intensity of 1.71 Mrad/hour, in quartz ampoules. The irradiated solid olefins (with the exception of *n*-decene-1) were amorphous. A DRSh-250 lamp served as the light source. Light filters were used to isolate separate regions of the spectrum. Irradiation with light and measurements of the EPR spectra were also carried out at the temperature of liquid nitrogen. The EPR spectra of γ-irradiated *n*-olefins, recorded 60 min after γ-irradiation, are shown in Fig. 1 (*a*) and (*b*), in

Fig. 2 (*a*), (*g*) and (*zh*), and in Fig. 3 (*a*) and (*b*). All spectra have eight poorly resolved hyperfine-structure lines: another spectrum with an odd number of li-

···of hfs, which worsens the resolution. In addition, in the EPR spectra of *n*-olefins with the double bond in the α-position, a narrow intense line is observed in the center of the spectrum. This line disappears upon irradiation with light of wavelength 5000 Å and shorter. It is not associated with the visible color centers, since the latter disappear upon irradiation with light with $\lambda = 7000$ Å. However, this line does not make a noticeable contribution to the total concentration of unpaired spins.

The yield of radicals in *n*-olefins with the double bond in the α-position, calculated from the areas of the EPR spectra, is 3–4 times smaller than with the double bond in the β-position. The approximate values of $G(R)$ are as follows: $G(R$-n-pentene-1)—1.6; $G(R$-n-pentene-2)—5.6; $G(R$-n-hexene-1)—1.3; $G(R$-n-hexene-2)—3.8.

Upon irradiation with light from a DRSh-250 lamp with a BS-8 filter ($\lambda \geq$ 3400 Å), all components of the previously poorly resolved eight-line spectrum of the γ-irradiated samples are distinctly resolved. The exposure time was several hours. The EPR spectra of all olefins (except *n*-pentene) after irradiation with light are characterized by a distribution of hfs-line intensities close to binomial. The distance between the components of the hfs of the resolved eight-line spectrum for all the *n*-olefins studied is ~ 23 gauss; the width of an individual component is ~ 10 gauss.

After the irradiation with light is stopped and the samples are kept in liquid nitrogen for several days, the eight-line spectrum again gradually changes into the original spectrum obtained after γ-irradiation. The rate of this process depends on the length of the molecular chain and decreases as it increases.

In all changes of the spectra, the total concentration of unpaired spins remains constant, with the exception of *n*-hexene-1 and 2 and *n*-heptene-1 and 2, in which the concentration of unpaired spins decreases somewhat upon prolonged storage in liquid nitrogen. The EPR spectra characterizing the reversible transformations of radicals described above in some of the olefins studied are shown in Fig. 1.

Fig. 2. EPR spectra: **a**—*n*-hexene-1 and **b**—*n*-heptene-2 immediately after γ-irradiation at 77°K; **c**, **d**—after storage in liquid nitrogen for 3–6 days.

As the analysis shows, the eight-line spectrum with a binomial distribution of intensities is a superposition of the spectra of two alkyl radicals:

$$\sim \mathrm{CH_2 - \dot{C}H - CH_2} \sim \tag{1}$$

with an intensity ratio 1 : 5 : 10 : 10 : 5 : 1, in which all hydrogen nuclei are equivalent, and of the radical

Fig. 3. EPR spectra: a —n-pentene-1, b —n-pentene-2 after γ-irradiation at 77° K; c, d —after subsequent irradiation with light (BS-8 filter) for 3 hours

Figure 2: Fig. 3. EPR spectra: a —n-pentene-1, b —n-pentene-2 after γ-irradiation at 77° K; c, d —after subsequent irradiation with light (BS-8 filter) for 3 hours

$$\sim \mathrm{CH_2 - \dot{C}H - CH_3} \tag{2}$$

with an intensity ratio $1 : 5 : 11 : 15 : 15 : 11 : 5 : 1$, in which for one of the β-hydrogens in the methylene group the splitting is approximately twice as large as for the remaining α- and β-hydrogens. In the resulting spectrum, the six-line spectrum is represented with a weight twice as large as that of the eight-line spectrum of the radical $\sim \mathrm{CH_2 - \dot{C}H - CH_3}$.

Spontaneous transformation of radicals during prolonged storage of γ-irradiated samples was also observed by us without preliminary···

exposure to light. This is seen by comparing the EPR spectra recorded immediately after γ-irradiation and after storage in liquid nitrogen for several tens of hours. This change in the spectra for two examples is shown in Fig. 2. The hfs lines of the eight-line spectrum of the alkyl radicals of *n*-pentene-1, *n*-hexene-1 and -2, and *n*-heptene-1 and -2 almost completely disappear upon storage in liquid nitrogen for four days. In the spectra of *n*-decene-1 and *n*-octene-1, such changes occur upon storage in liquid nitrogen for several weeks. Thus, during prolonged storage in liquid nitrogen after γ-irradiation, a spontaneous conversion of alkyl radicals into allyl radicals occurs, just as after irradiation with light. These conclusions, as in the case of polymers ([1]), can be interpreted as the result of migration of the free valence (and, correspondingly, in the opposite direction, of hydrogen atoms) along the molecular chain. The fact that in hydrocarbons with a longer molecular chain the process of formation of the allyl radical occurs more slowly is evidently associated with a greater migration path length of the unpaired electron to the double bond, since the initial position of the unpaired electron is, on average, farther from the double bond the longer the molecular chain. The fact that migration proceeds from the double bond is confirmed by experiments with *n*-paraffins. Upon irradiation with light of γ-irradiated paraffins (hexadecane, decane, etc.), no changes occur in the EPR spectra.

Fig. 3. EPR spectra: *a* —*n*-pentene-1, *b* —*n*-pentene-2 after γ-irradiation at 77° K; *c*, *d* —after subsequent irradiation with light (BS-8 filter) for 3 hours

The EPR spectra of γ-irradiated *n*-pentene-1, *n*-hexene-1 and -2, and *n*-heptene-1 and -2 that had been stored in liquid nitrogen apparently represent a superposition of the spectra of several allyl radicals of different structure with an odd number of hfs lines, the radical

$$CH_2 = CH - \dot{C}H - CH_2 \sim, \tag{3}$$

which gives an odd number of lines, 5 or 7 (if one of the β-hydrogens of the methylene group does not interact with the unpaired electron, or if the splitting on one of the β-hydrogens of the CH_2 group is twice as large as on the other α- and β-hydrogens), and the radical

$$CH_3 - CH = CH - \dot{C}H - CH_2 \sim, \tag{4}$$

which gives an odd number of lines if one of the β-hydrogens in the CH_2 group is nonequivalent. The presence, with small weight, of allyl radicals with an even number of hfs lines (all hydrogens equivalent) is also possible. This is indicated by the fact that if n-decene-1 is heated to a temperature of $-85°$ and the spectrum is then recorded at the temperature of liquid nitrogen, a poorly resolved spectrum with six or eight hfs lines is observed, with splitting of ~ 16 gauss.

Further confirmation of the migration mechanism of radical transformation under the action of light was also provided by the following experiments. If the action of light is associated

with migration of the free valence from the double bond, then in γ-irradiated n-pentene-2, in contrast to n-pentene-1, an eight-line EPR spectrum should not be observed, since in n-pentene-2 the only position to which the free valence can move from the double bond is the terminal group $-CH_3$. However, the spectrum of the radical $CH_3CHCHCH_2\dot{C}H_2$ may have 8 hfs lines. Indeed, prolonged exposure of γ-irradiated n-pentene-2 to light did not lead to the appearance of an eight-line EPR spectrum, as was the case in other n-olefins (Fig. 3).

It follows from the foregoing that the migration of the free valence along the molecular chain in stabilized polymer radicals, established by us earlier ([1]), is not specific only to polymers, but may also occur in radicals formed upon γ-irradiation of ordinary molecules.

Apparently, the processes described can play an essential role in various reactions under the action of radiation, or in other chemical reactions proceeding with the participation of free radicals.

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