A study of alkyl radicals in the matrix of polycrystalline *n*-alkane γ-irradiated at 77 K

1. Effect of chain length on ESR spectra of γ-irradiated linear alkanes

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The composition of alkyl radicals (AR) formed by γ-radiolysis ($T = 77$ K) of polycrystalline *n*-alkanes with different lengths of the carbon chain (C(5), C(7), C(10), C(11), and C(18)) and their polymeric analog (polyethylene) was estimated from the ESR spectra. The ESR spectra of the irradiated *n*-alkanes are superpositions of the signals from the $H_3CC^{\cdot}HCH_2$– and ~$CH_2C^{\cdot}HCH_2$~ radicals, whose HFS constants with α and β protons as well as the equilibrium conformation are independent of the chain length of the *n*-alkane molecule. A dependence of the concentration of the radicals on the chain length of *n*-alkane was found. The absence of the ~$CH_2C^{\cdot}H_2$ radicals that may arise upon H atom elimination from the Me fragments of the *n*-alkane molecules is most likely related to the transfer of excitation energy from the Me group to the neighboring methylene fragment and the transformation of the ~$CH_2C^{\cdot}H_2$ radicals into $H_3CC^{\cdot}HCH_2$~ radicals. With account for this, the concentrations of the AR formed were suggested to be proportional to the number of H atoms at the corresponding C atom.

Key words: polycrystalline *n*-alkanes, polyethylene, γ-radiolysis, distribution of radicals, ESR spectroscopy.

Hyperfine structure (HFS) of the ESR spectrum of alkyl radicals (AR) in the solid phase reflects the interaction of an unpaired electron with the nearest environment only. In these ESR spectra, the values of HFC constants with γ-protons do not exceed 0.05 mT,[1] which is much less than the half-width of the spectral components (~1.0 mT)[2] and, as a rule, they cannot be detected. Therefore, HFS of ESR spectra of AR is the result of the interactions of an unpaired electron with α- and β-protons only. As a result, only AR with the free valence at the C atoms in positions 1, 2, or 3 can be distinguished in the solid phase from ESR spectra. Therefore, the composition of AR formed during γ-radiolysis of *n*-alkanes can unambiguously be determined from the ESR spectra of the latter only for molecules with a chain length of at most five C atoms. In the case of *n*-alkanes with a longer chain, the AR composition can be established indirectly. For this purpose, one should know how the carbon chain length of the *n*-alkane molecule affects the composition of radicals formed under its radiolysis.

Although numerous data have been obtained by the ESR study of irradiated solid organic substances,[2] the quantitative composition of AR and its dependence on the chain length of the linear alkane are virtually unstudied.

This work is devoted to the ESR study of radicals formed under γ-radiolysis of polycrystalline linear alkanes with different chain lengths.

Experimental

Linear alkanes *n*-C_5H_{12}, *n*-C_7H_{16}, *n*-$C_{10}H_{22}$, and *n*-$C_{18}H_{38}$ (content of the main substance ≥99.95%) and their high-molecular analog, a low-pressure polyethylene (PE) powder, were used.

Radiolysis of samples (^{60}Co γ-radiation, dose of irradiation power 28 Gy s^{-1}) was carried out in tubes of SK-4B glass *in vacuo* at 77 K. ESR spectra were recorded on a PS100.Kh 3-cm radiospectrometer.

ESR spectra of radicals were simulated using the EPRTOOLS program (version 3, developed at the Scientific Technical Cooperative Center for Radiospectroscopic Instrument-making "Tsentrospektr," Minsk).

Results and Discussion

The shape of ESR spectra of irradiated polycrystalline samples of linear alkanes depends, to a great extent, on the chain length of the alkane molecule. When the chain gradually elongates, the seven-component spectrum transforms into the six-component spectrum. The ESR spectra of *n*-alkanes γ-irradiated at 77 K are presented in Fig. 1 (spectra *3*—*8*). The theoretical spectra of $H_3CC^{\cdot}HCH_2$– and ~$H_2CC^{\cdot}HCH_2$~ corresponding to the seven- and six-component spectra were obtained by the simulation of the experimental spectra of irradiated *n*-alkanes (see Fig. 1, spectrum *2*, Table 1). The

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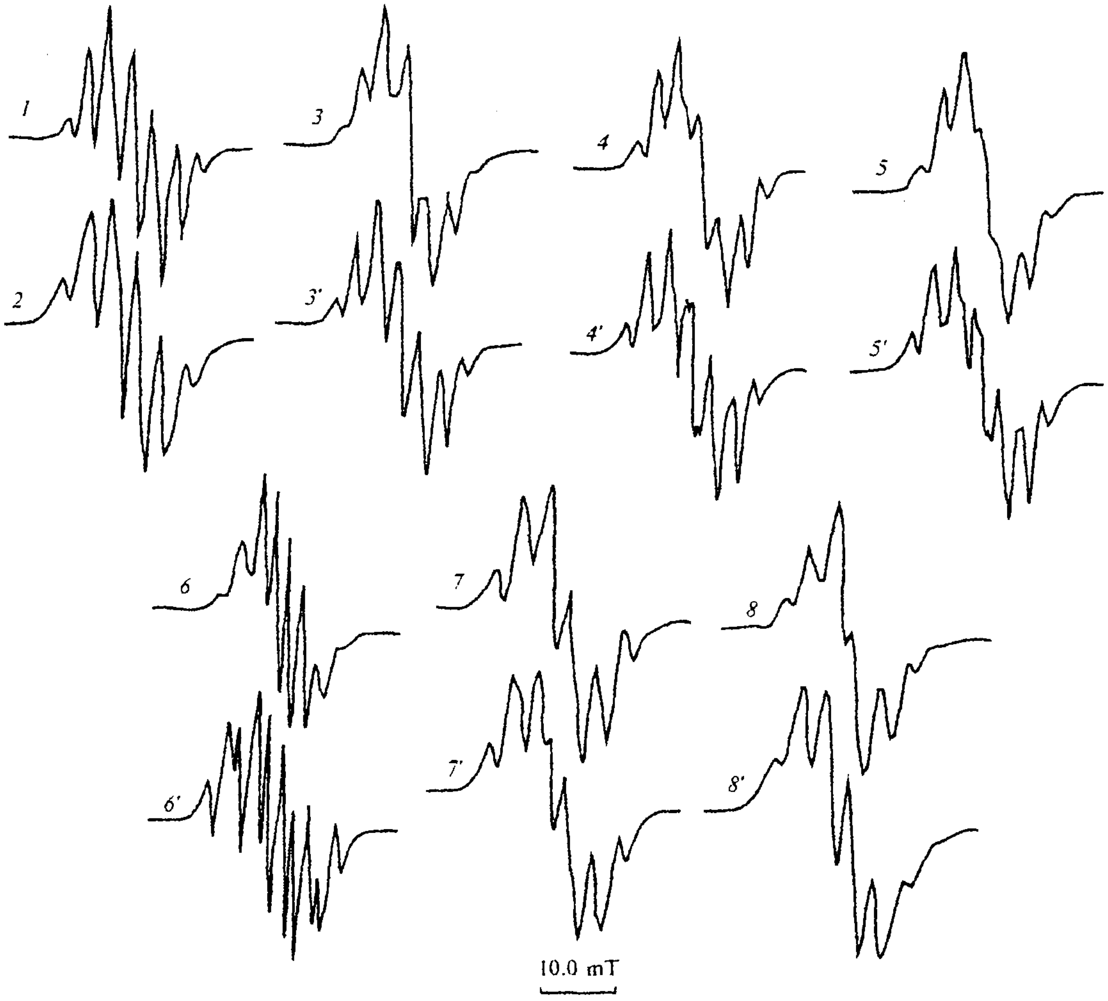

Fig. 1. Theoretical ESR spectra of $H_3CC^{\cdot}HCH_2$– (*1*) and –$CH_2C^{\cdot}HCH_2$– radicals (*2*); experimental (*3*—*8*) and theoretical (*3'*—*8'*) ESR spectra of *n*-C_5H_{12} (*3*, *3'*), *n*-C_7H_{16} (*4*, *4'*), *n*-$C_{10}H_{22}$ (*5*, *5'*), *n*-$C_{11}H_{24}$ (*6* (Ref. 3), *6'*), *n*-$C_{18}H_{38}$ (*7*, *7'*), and PE (*8*, *8'*) γ-irradiated at 77 K with a dose of 30 kGy.

Table 1. Parameters of the ESR spectra and equilibrium conformation of alkyl radicals formed under γ-radiolysis of *n*-alkanes at 77 K

Radical	HFC constants/mT						Angle /deg*	
	a_α^H	$a_{CH_3}^H$	$a_{CH_2}^{H(1)}$	$a_{CH_2}^{H(2)}$	$a_{CH_2}^{H(3)}$	$a_{CH_2}^{H(4)}$	θ_1	θ_2
$H_3CC^{\cdot}HCH_2$–, R_2	2.4	2.55	3.8	3.3			26	34
–$CH_2C^{\cdot}HCH_2$–, R_m	2.2		3.56	3.56	3.56	3.56	30	30

* The angle between the projection of the C_β—H bond of the methylene fragment of the radical and the axis of the orbital of an unpaired electron.

$H_3CC^{\cdot}HCH_2$– radical (R_2) is formed when the H atom is eliminated from the second C atom of the *n*-alkane molecule. The HFC constants obtained for this radical agree well with the parameters of these radicals stabilized in single crystals of *n*-alkanes irradiated at 77 K.[3] As follows from Table 1, in the –$CH_2C^{\cdot}HCH_2$– (R_m) radical, all four H_β atoms are equivalent. The HFC constants with these protons are equal to ~3.56 mT. The

HFC constants close to this value have been obtained by examination of the spectra of the $\sim CH_2\dot{C}HCH_2\sim$ radicals stabilized in PE.[4–6]

Examination of the ESR spectra of γ-irradiated *n*-alkanes shows that they mainly represent a superposition of signals from the R_2 and R_m radicals. On going from one alkane to another, the main parameters of the ESR spectrum of these radicals (HFC constants with α- and β-protons) remain unchanged. However, the linewidths in the ESR spectra of the R_2 and R_m radicals can differ (Table 2). For example, in the theoretical spectrum of *n*-undecane (see Fig. 1, spectrum *6'*), the lines of the R_m radical are more narrow than those in the spectra of other alkanes. This results in a substantial distinction of the spectrum of *n*-undecane from the spectra of other *n*-alkanes (see Fig. 1). Thus, the observed distinction in the spectrum of *n*-undecane can be explained by a decrease in the ESR linewidths.

The HFC constants with α-protons for the $H_3C\dot{C}HCH_2\sim$ and $\sim CH_2\dot{C}HCH_2\sim$ radicals (2.4 and 2.2 mT, respectively) coincide well with known values.[1] In alkyl radicals where the motion around the $C_\alpha—C_\beta$ bond is retarded, the HFC with the β-proton depends on the geometry of the radical (the angle of rotation about the $C_\alpha—C_\beta$ bond) and is described by the formula

$$a_\beta^H = B_1\rho_\alpha + B_2\rho_\alpha\cos^2\theta, \qquad (1)$$

where B_1 = 0.38 mT, B_2 = 5.1 mT; ρ_α is the spin density on the C atom C_α; and θ is the angle between the projection of the $C_\beta—H$ bond and the axis of the orbital of an unpaired electron.[7,8] The parameters of the R_2 and R_m radicals presented in Table 1 are well described by Eq. (1). Since the HFC constants with β-protons of these radicals are independent of the length of the hydrocarbon chain and elongation of the latter to approximate the PE macromolecule exerts almost no effect on the parameters of the ESR spectra, the equilibrium conformation of the R_2 and R_m radicals should also be independent of the chain length of the *n*-alkane molecule.

We found that a strictly specified quantitative correlation between the concentrations of the R_2 and R_m radicals was fulfilled for γ-radiolysis of polycrystalline *n*-alkanes. The ratio of the concentrations of these radicals in the theoretical spectra of *n*-alkanes irradiated at 77 K are presented in Table 2. It follows from these data that the ratio of concentrations of the R_2 and R_m radicals depends on the alkane chain length. In the case of *n*-pentane (see Fig. 1, spectra *3* and *3'*), the seven-component ESR spectrum is mainly observed, which is attributed to the $H_3C\dot{C}H(CH_2)_2Me$ radical, whose concentration is fivefold higher than that of the $HC[CH_2Me]_2$ radicals. An inverse ratio of concentrations of the R_2 and R_m radicals (5 : 14) is observed for the samples of γ-irradiated *n*-octadecane. In the case of *n*-octadecane (see Fig. 1, spectra *7* and *7'*), the content of the R_2 radicals ($H_3C\dot{C}HCH_2(CH_2)_{14}Me$) is almost threefold lower than that of the $\sim CH_2\dot{C}HCH_2\sim$ radicals. In turn, the ESR spectra of irradiated *n*-$C_{10}H_{22}$ and *n*-$C_{11}H_{24}$ contain signals from the R_2 and R_m radicals with a close intensity. Since the spectra of the R_m (see Fig. 1, spectrum *2*) and R_2 radicals (see Fig. 1, spectrum *1*) substantially differ, the shape of the spectrum of irradiated *n*-alkane, being a superposition of signals from these radicals, is determined by the relative concentration of the latter.

Table 2. Parameters of the theoretical spectra that most well describe the experimental ESR spectra of *n*-alkanes irradiated at 77 K

Alkane	R_2 : R_m	*h**/mT	
		R_2	R_m
n-C_5H_{12}	5 : 1	1.2	1.6
n-C_7H_{16}	5 : 3	1.0	1.6
n-$C_{10}H_{22}$	5 : 6	1.0	1.8
n-$C_{11}H_{24}$	5 : 7	1.0	1.0
n-$C_{18}H_{38}$	5 : 14	1.2	1.6
PE	0 : 1		2.0

* *h* is the half-width of spectral lines.

Thus, the main portion of radicals formed upon γ-radiolysis of polycrystalline short-chain *n*-alkanes comprises R_2 radicals whose free valence is localized at the second C atom. The R_m radicals ($\sim CH_2\dot{C}HCH_2\sim$) are mainly observed in the radiolysis of *n*-alkanes with a longer chain at 77 K. With a gradual elongation of the chain of the *n*-alkane molecule, the fraction of the R_m radicals increases in the ESR spectrum, and the latter transforms from the seven-component into the six-component spectrum. These changes in the ESR spectra on going from high-molecular paraffin or PE to lower-molecular *n*-dodecane are explained[9] by the transition of the R_m radical from one conformation to another. However, our analysis showed that the observed changes were related to distinctions in the quantitative ratio between concentrations of the R_2 and R_m radicals rather than to the conformational peculiarities of the R_m radicals.

Let us consider the ratio of concentrations of the alkyl radicals as a function of the chain length of the molecule of irradiated *n*-alkanes. We can suggest that the distribution of the alkyl radicals R_1, R_2, R_3, ..., R_n formed by γ-radiolysis of a polycrystalline *n*-alkane due to the elimination of the H atom from the first, second, third, and *n*th C atom corresponds to the equiprobable abstraction of the H atom from any C atom. In this case, the concentrations of the radicals with different structures should be proportional to the number of H atoms at the corresponding C atoms in the *n*-alkane molecule. For example, for *n*-pentane, the ratio of concentrations of the radicals should be the following:

$$R_1 : R_2 : R_3 = 3 : 2 : 1. \qquad (2)$$

The R_1 radical is not detected experimentally, and the ratio of concentrations of the observed radicals R_2 and R_3 should be 2 : 1. The experimental ratio of concentrations of these radicals is 5 : 1 (see Table 2). Since three units, by which the concentration of the R_2 pentyl radicals increases, are equal to the fraction of the R_1 radicals in Eq. (2), we may assume that during γ-radiolysis of *n*-pentane at 77 K the R_1 radicals are transformed into R_2. Most likely, this transition occurs before the formation of the R_1 radical and is a result of the transfer of the excitation energy of the Me group to the adjacent CH_2 fragment. The possibility of this energy transfer during radiolysis of the *n*-alkane molecule has been observed previously.[10] Analysis of the ESR spectra of other *n*-alkanes irradiated at 77 K also indicates an increase in the concentrations of the R_2 radicals at the expense of the R_1 radicals. The ratio of the radical concentrations in the theoretical spectra (see Fig. 1, spectra *3'—7'*), which optimally describe the experimental ESR spectra of the corresponding irradiated *n*-alkanes (see Fig. 1, spectra *3—7*), is presented in Table 2. The concentrations of the alkyl radicals R_1, R_2, ..., R_n (taking into account the transformation of the R_1 radicals into R_2) are proportional to the number of H atoms at the C atoms in the *n*-alkane molecule. As follows from the data in Table 2, the concentrations of the alkyl radicals formed by γ-radiolysis of polycrystalline *n*-alkanes whose molecules contain more than four C atoms are described by the ratio $[H_3CC^{\cdot}HCH_2]/[\sim CH_2C^{\cdot}HCH_2\sim] \approx 5/(n-4)$, where n is the number of C atoms in the *n*-alkane molecule.

Thus, the observed deviation from the primary distribution of radicals proportional to the number of H atoms at the C atoms of the *n*-alkane molecule is most likely associated with the transfer of the excitation energy of the CH_3 group to the adjacent methylene fragment.

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