

# An ESR study and quantum-chemical calculations of alkyl radicals in the matrix of polycrystalline *n*-alkane and *n*-perfluoroalkane irradiated at 77 K. Effect of intermolecular interactions and carbon chain length on the radical formation.

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The composition of alkyl radicals (AR) formed by  $\gamma$ -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  $\text{H}_3\text{CC}\dot{\text{C}}\text{HCH}_2\sim$  and  $\sim\text{CH}_2\text{C}\dot{\text{C}}\text{HCH}_2\sim$  radicals, whose HFS constants with  $\alpha$  and  $\beta$  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  $\sim\text{CH}_2\text{C}\dot{\text{C}}\text{H}_2$  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  $\sim\text{CH}_2\text{C}\dot{\text{C}}\text{H}_2$  radicals into  $\text{H}_3\text{CC}\dot{\text{C}}\text{HCH}_2\sim$  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. To reveal the reasons for the previously found absence of end radicals upon  $\gamma$ -radiolysis of *n*-alkane polycrystals, we performed quantum-chemical calculations (SCF-MO, RHF, 6-31G\* basis set) of the *n*-heptane molecule and its four radicals. The energies of the crystal lattice were calculated by the atom-atom potential method. Comparison of the experimental and calculated data showed that the absence of the end radicals is not related to the intermolecular interaction in the crystals. The most probable reason for the selective radical formation upon radiolysis can be a transfer of the excitation energy within the *n*-heptane molecule occurring before the radical formation. Alkyl radicals in the matrix of polycrystalline *n*-perfluoroalkane irradiated at 77 K were investigated by ESR method and quantum-chemical calculations. Also were explored effect of intermolecular interactions and carbon chain length on the radical formation under radiolysis perfluoroalkanes and polytetrafluoroethylene. An equilibrium conformation of the  $\sim\text{F}_2\text{CF}_2\text{C}\bullet$  and  $\sim\text{F}_2\text{CFC}\bullet\text{CF}_2\sim$  radicals stabilized in matrices of polytetrafluoroethylene and *n*-perfluoroalkanes was studied. Upon cooling from 300 to 77 K at temperatures below 200 K, the ESR

spectrum of this radical changes, and the well resolved hyperfine structure appears. The hyperfine splitting constants on nuclei of two nonequivalent  $F_{\beta}$  atoms of  $\sim F_2CFC\bullet$  radicals were determined: 2.2 and 1.1 mT, respectively. The  $A_{\parallel}$  and  $A_{\perp}$  values for the  $F_{\alpha}$  atoms are 22.5 and 3.3 mT, respectively. The conformational angle between the axis of the orbital of an unpaired electron and projection of the  $C_{\beta}-C_{\gamma}$  bond is  $5.6^{\circ}$ . Found are the hyperfine splitting constants for  $\alpha$  and  $\beta$  fluorine atoms in the  $\sim F_2CFC\bullet CF_2\sim$  radical stabilized in crystal matrix of n-PFA. Russian Fund for Fundamental Research has supported this work cod No: 01-01-97006.