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

2.* Effect of intra- and intermolecular interactions on radical formation in *n*-heptane polycrystals

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To reveal the reasons for the previously found absence of end radicals upon γ-radiolysis of *n*-heptane 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.

Key words: polycrystalline *n*-heptane, alkyl radicals, quantum-chemical calculations, atom-atom potentials.

It has been shown in the previous work[1] that γ-radiolysis of polycrystalline *n*-heptane (Fig. 1, *a*) affords three types of radicals, in which an unpaired electron is localized on the second (R_2), third (R_3), and fourth (R_4) C atoms (see Fig. 1, *c—e*), and no radicals with an unpaired electron on the first C atom (R_1) (see Fig. 1, *b*) were observed. This experimental result seems unusual, because the fractions of the radicals with different structures, seemingly, should be proportional to the number of H atoms at the C atoms.

To explain these data, we proposed three hypotheses. This work is devoted to the verification of the hypotheses. The first of them is based on different stabilities of the radicals. According to the X-ray diffraction analysis (XDA) data for the *n*-C_7H_{16} crystals,[2] the *n*-heptane molecules in the solid state have no shortened intermolecular contacts, *i.e.*, in fact, they are isolated. The weakness of intermolecular interactions is also indicated by the low melting point of the *n*-heptane crystals (184.2 K). This agrees with our calculation of the energy of the crystalline lattice of *n*-heptane (−15.8 kcal mol^{-1}). It is known that it is by 2—3 times higher[3,4] for crystals with a melting point of 353—373 K. Therefore, intermolecular interactions cannot affect the stability of the *n*-heptane radicals in the crystal, *i.e.*, the "gas phase approximation" is appropriate for its estimation.

The second hypothesis assumes the steric predeterminacy of radical formation due to the spatial packing of the *n*-alkane molecules in the crystal. The third hypothesis supposes a possibility of transition of the arisen free valence (FV) from one C atom to another, and the migration of FV in the alkyl radical can be both intra- and intermolecular.

The well-known, first advanced in Ref. 5 transfer of the H atom occurs by the following reaction:

$$R_0H + R^{\cdot} \longrightarrow R_0^{\cdot} + RH.$$

The transfer of FV occurs during isomerization of the radical, *i.e.*, during its intramolecular rearrangement, for example, according to the scheme

$$\sim CH_2CH_2C^{\cdot}HCH_2\sim \longrightarrow \sim CH_2C^{\cdot}HCH_2CH_2\sim.$$

Migration of FV has previously[6,7] been explained by the decomposition of the system accompanied by the elimination of any molecular fragment from the end radical.

In this work, we compared the ESR spectra with the results of quantum-chemical calculations of the R_1, R_2, R_3, and R_4 radicals to interpret the selectivity of radical formation during radiolysis of *n*-heptane polycrystals. In addition, we estimated the energies of the crystalline lattice of nonirradiated *n*-heptane and model crystals with the R_1, R_2, R_3, and R_4 radicals.

Quantum-chemical calculations

Nonempirical quantum-chemical calculations of the *n*-C_7H_{16} molecule (see Fig. 1, *a*) were performed by the RHF/6-31G* method, and the R_1, R_2, R_3, and R_4 radicals (see Fig. 1, *b—e*) were calculated in the UHF approximation in the 6-31G* basis set using the GAMESS program[8] with the complete optimization of geometry. It is known[9] that the quantum-chemically calculated geometry of radicals is very sensitive to

* For Part 1, see Ref. 1.

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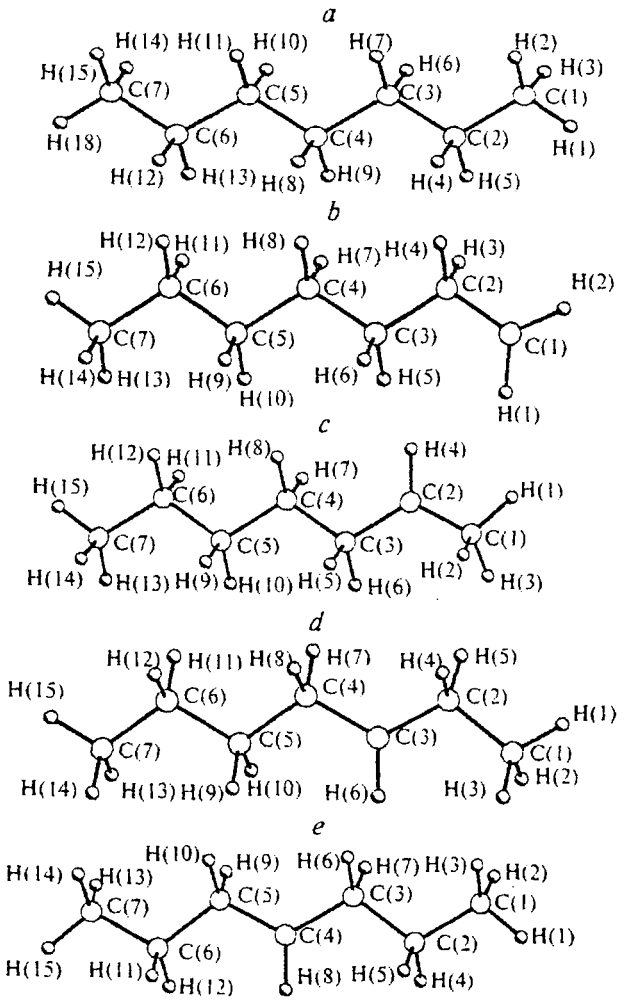

Fig. 1. Structures of the *n*-heptane molecule (*a*) and radicals R_1 (*b*), R_2 (*c*), R_3 (*d*), and R_4 (*e*) with numeration of the atoms.

the choice of the basis set. Comparison of the results obtained with the 3-21G, 4-31G, and 6-31G* basis sets showed that the structure of the *n*-heptane molecule is well reproduced in all cases, and that of the radicals is reproduced only in the 6-31G* basis set. Coincidence of the experimental and calculated data on the conformation of the radical served as a criterion for the validity of the structure found.

It is known that the equilibrium conformation of a radical, *i.e.*, mutual arrangement of substituents at the C_α and C_β atoms, can be established from the ESR spectra, using the angular dependence of the hyperfine splitting on the β-protons:

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

where $B_1 = 0.38$ mT, $B_2 = 5.1$ mT; ρ_α is the spin population of the $2p_\pi$-AO of the α-C atom; θ is the angle of deviation of the C_β—H bond from the plane containing this AO and the C_α—C_β bond.[10,11] For the R_2 radical, the splittings on protons are the following: $a_\alpha^H = 2.4$ mT, $a_{Me}^H = 2.55$ mT, $a_{\beta1}^H = 3.3$ mT, and $a_{\beta2}^H = 3.8$ mT[1]; whereas those for R_3 and R_4 are $a_\alpha^H = 2.4$ mT, $a_{\beta1}^H = a_{\beta2}^H = a_{\beta3}^H = a_{\beta4}^H \cong 3.56$ mT.[1] These splittings are satisfactorily described by Eq. (1), which makes it possible to determine the equilibrium conformations of the radicals in the crystalline matrix of irradiated *n*-heptane.

The Newman projections along the C(2)—C(3) (*a*), C(3)—C(2) (*b*), and C(4)—C(3) (*c*) bonds in the radicals R_2, R_3, and R_4, respectively, are presented in Fig. 2. As follows from the experimental data, the R_3 and R_4 radicals have a planar conformation of the C(3) and C(4) atoms bearing unpaired electrons with *trans*-orientation of the C—C bonds and the same angles θ_1 and θ_2 (30° from the ESR spectra, 29.0—31.1° from the nonempirical quantum-chemical calculations in the 6-31G* basis set). For the R_2 radical, we observed a slight deviation from this conformation: $\theta_1 = 26°$, $\theta_2 = 34°$ from the ESR spectra and $\theta_1 = 32.2°$, $\theta_2 = 32.6°$ from the similar calculation. Good coincidence of the experimental and calculated values indicates that the real structure of the R_2, R_3, and R_4 radicals in polycrystals is reproduced. Therefore, we preferred the 6-31G* basis set. The bond lengths and bond angles obtained in this basis set for the *n*-heptane molecule and R_1, R_2, R_3, and R_4 radicals are presented in Tables 1 and 2.

It is known[12] that in the R_4 radical the interaction of hydrogen atoms of the Me groups with the substituents at the C atom is small and the barrier of rotation of the Me groups does not exceed 0.1 kcal mol^{-1}, *i.e.*, at 77 K rotation can be considered free. In this case, the averaged hyperfine splitting for protons of the Me groups of the R_4 radical should be 2.48 mT. The observed value of this splitting (2.55 mT) only slightly differs from the calculated value.

Semiempirical quantum-chemical calculations were performed with the complete optimization of the geometry and taking into account the configurational interaction by the MNDO, AM1, and PM3 methods using the MOPAC-7 complex of programs.[13] The main purpose of these calculations is to choose the approximation that correctly reflects the structure of *n*-heptane and its radicals. The results showed that the bond lengths and bond angles of the *n*-heptane molecule calculated in terms of the MNDO, AM1, and PM3 schemes agree well with the experimental values. For the radicals, we observed a good coincidence of the experimental and calculated values of torsion angles H—C—C—H and spin populations of the sp^2-hybridized C atoms; however, in all semiempirical approximations, we obtained shortening of the $C(sp^3)$—$C(sp^3)$ and especially

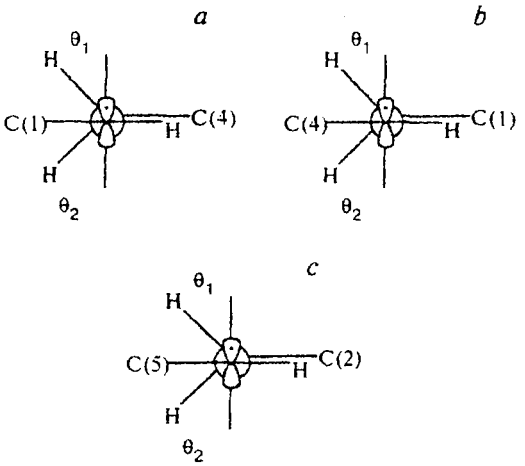

Fig. 2. The Newman projections along the C(2)—C(3) bonds in R_2 (*a*), C(3)—C(2) in R_3 (*b*), and C(4)—C(4) in R_4 (*c*); θ_1 and θ_2 are the angles between the $2p_\pi$-AO axis of the unpaired electron and C—H bonds.

Table 1. Bond lengths (d) and bond angles (ω) of the n-heptane molecule according to the data of XDA (I), nonempirical (II) and semiempirical (III) calculations. For the XDA data, errors in determination of the parameters are indicated in parentheses

Bond	d/Å		
	I	II	III
C(1)—C(2)	1.531(2)	1.526	1.512
C(2)—C(3)	1.525(2)	1.528	1.520
C(3)—C(4)	1.532(2)	1.528	1.520
C(4)—C(5)	1.527(2)	1.528	1.520
C(5)—C(6)	1.532(2)	1.528	1.520
C(6)—C(7)	1.522(2)	1.526	1.512
C—H [a]	0.99(1)—1.00(1)	1.085	1.097—1.098
C—H [b]	0.99(1)—1.00(1)	1.087—1.088	1.108
Angle	**ω/deg**		
	I	II	III
C(1)—C(2)—C(3)	112.7(3)	113.0	111.5
C(2)—C(3)—C(4)	113.6(3)	113.4	111.4
C(3)—C(4)—C(5)	113.1(3)	113.3	111.3
C(4)—C(5)—C(6)	113.5(3)	113.4	111.4
C(5)—C(6)—C(7)	112.9(3)	113.0	111.5
C—C—H [a]	108(1)—109(1)	111.1—111.3	111.2—111.7
C—C—H [b]	108(1)—109(1)	109.2—109.4	109.9—110.0

[a] Bonds and bond angles in the $-CH_3$ groups.
[b] Bonds and bond angles in the $>CH_2$ groups.

$C(sp^3)—C(sp^2)$ bond lengths as compared to the standard values (1.54 and 1.50 Å; see Table 2). The least divergences were obtained by the PM3 method, and hence, its use in the calculations of more complex radicals of n-alkanes is preferential.

The n-heptane molecule in the excited state was calculated by the GAMESS program in the 6-31G* basis set. All quantum-chemical calculations were performed on an RM600 computer at the Computer Center of the Institute of Problems of Chemical Physics of the Russian Academy of Sciences.

Calculations by the atom-atom potential method (AAP) were performed by the PMC program[14] using the 6-exp parameters.[15] Taking into account the Coulomb repulsions, we accepted the charges on the atoms calculated for the R_1, R_2, R_3, and R_4 radicals in the 6-31G* basis set. It is seen from the data presented in Table 1 that the calculated bond lengths and bond angles slightly differ from the values obtained by XDA of n-heptane crystals. These distinctions have almost no effect on the estimated energy of the crystalline lattice: −15.8 and −15.7 kcal mol^{-1} for the crystal with the parameters from the nonempirical quantum-chemical calculation and XDA data, respectively.

Results and Discussion

The quantum-chemical calculations for the R_1, R_2, R_3, and R_4 radicals (see Fig. 1) showed that the total energies of all the radicals are almost the same (Table 3): the highest difference between them does not exceed 2.3 kcal mol^{-1} in the nonempirical calculation scheme and 3.5 kcal mol^{-1} in the semiempirical variants. Such low differences in energies do not allow one to speak with confidence about a higher stability of any of these radicals. Nevertheless, the R_1 radical differs from the others in electronic structure: in it the spin density on the sp^2-hybridized C atom is elevated and its singly occupied molecular orbital (SOMO) has a lower energy (see Table 3). This suggests that the absence of end radicals R_1 in the irradiated polycrystalline n-heptane cannot be explained only by their low stability.

To verify the second assumption, we calculated the energy of the crystalline lattices of n-heptane and hypothetical systems consisting of the $R_1—R_4$ radicals. We assumed that changes in the conformation of the n-heptane molecules during the radical formation destabilize the crystal structure in different ways. According to the experimental and calculated data, *trans*-orientation of the C atoms relative to each other is observed in the molecules and radicals (all torsion C—C—C—C angles amount to ~180°). When the radicals form, the torsion angles $H—C(sp^2)—C(sp^3)—C(sp^3)$ change (from ±60° in the n-heptane molecule to ~0° in the $R_1—R_4$ radicals). In the calculations by the atom-atom potential method, we simulated the influence of intramolecular changes on the crystalline lattice energy and obtained the following results: the energy of the crystalline lattice of n-heptane is −15.8 kcal mol^{-1} and those of the hypothetical systems consisting of the R_1, R_2, R_3, and R_4 radicals are −14.3, −15.5, −15.0, and −12.6 kcal mol^{-1}, respectively. Thus, the substitution of the n-heptane molecules by the R_1, R_2, R_3, and R_4 radicals destabilizes the crystal, which is most pronounced in the case of the isomeric forms of R_1 and R_4 (by 1.5 and 3.2 kcal mol^{-1}, respectively). Since the R_1 radicals, unlike R_4, were not observed in the irradiated polycrystals of n-heptane, we may assume that a relation between the destabilization of the crystalline lattice and the selectivity of the formation of radicals in it during radiolysis is improbable.

Let us consider the possibility of transition of the arisen FV from one C atom of n-heptane to another. According to estimations,[5] the activation energy of the intermolecular process

$$R_oH + R^{\cdot} \longrightarrow R_o^{\cdot} + RH$$

is too high for its noticeable competition in the solid state with the intramolecular "jump" of the H atom:

$$\sim CH_2CH_2C^{\cdot}HCH_2\sim \longrightarrow \sim CH_2C^{\cdot}HCH_2CH_2\sim.$$

Therefore, during the solid state low-temperature radiolysis of n-heptane the intermolecular migration of FV in the reaction

$$n\text{-}C_7H_{16} + C^{\cdot}H_2(CH_2)_5Me \longrightarrow$$
$$\longrightarrow MeC^{\cdot}H(CH_2)_4Me + Me(CH_2)_5Me$$

is improbable. The transition $R_1 \rightarrow R_2$ in the irradiated n-heptane could occur due to the intramolecular rearrangement of the R_1 radical according to the scheme:

$$^{\cdot}CH_2(CH_2)_5Me \longrightarrow MeC^{\cdot}H(CH_2)_4Me.$$

Table 2. Bond lengths (d) and bond angles (ω) of the R_1, R_2, R_3, and R_4 radicals by the data of nonempirical (I) and semiempirical (II) calculations

Parameter	R_1		R_2		R_3		R_4	
	I	II	I	II	I	II	I	II
Bond				d/Å				
C(1)—C(2)	1.500	1.465	1.499	1.465	1.530	1.513	1.538	1.513
C(2)—C(3)	1.531	1.521	1.501	1.470	1.502	1.473	1.532	1.523
C(3)—C(4)	1.530	1.519	1.531	1.521	1.502	1.472	1.503	1.472
C(4)—C(5)	1.530	1.520	1.529	1.519	1.532	1.521	1.502	1.472
C(5)—C(6)	1.530	1.521	1.531	1.520	1.531	1.520	1.532	1.520
C(6)—C(7)	1.527	1.512	1.527	1.125	1.528	1.512	1.527	1.511
C—H [a]	1.085—1.087	1.097—1.098	1.086—1.090	1.097—1.098	1.086—1.087	1.097—1.098	1.086—1.087	1.097—1.098
C—H [b]	1.087—1.091	1.108—1.109	1.088—1.092	1.108—1.109	1.088—1.092	1.108—1.109	1.087—1.093	1.107—1.109
C—H [c]	1.085	1.081	1.084	1.092	1.076	1.092	1.076	1.092
Angle				ω/deg				
C(1)—C(2)—C(3)	113.2	112.7	121.4	120.5	113.2	112.5	113.3	111.3
C(2)—C(3)—C(4)	113.3	111.3	113.3	112.5	121.7	119.6	113.4	112.4
C(3)—C(4)—C(5)	113.2	111.4	113.7	111.3	113.5	112.3	121.8	119.5
C(4)—C(5)—C(6)	113.3	111.4	113.2	111.4	113.5	111.4	113.4	112.5
C(5)—C(6)—C(7)	113.1	111.4	113.3	111.4	113.0	111.5	113.4	111.6
C—C—H [a]	111.1—111.4	111.3—111.6	111.2—111.7	111.2—112.9	111.1—111.3	111.2—111.7	111.0—111.3	111.3—111.7
C—C—H [b]	109.2—109.4	109.9—110.1	109.2—109.3	109.8—110.4	109.1—109.9	108.6—110.3	109.0—109.8	108.8—110.3
C—C—H [c]	120.7, 121.4	120.6, 122.0	119.2	120.2	119.2	120.3	119.0	120.2

[a] Bonds and bond angles in the $-CH_3$ groups.
[b] Bonds and bond angles in the $>CH_2$ groups.
[c] Bonds and bond angles in the >CH group.

Table 3. Results of nonempirical calculations of the R_1, R_2, R_3, and R_4 radicals and n-heptane molecule RH in the excited state

Parameter	R_1	R_2	R_3	R_4	RH
E/au	−273.7657	−273.7693	−273.7691	−273.7692	−274.0217
E_{rel}/kcal mol^{-1}	2.3	0	0.1	0.1	
μ/D	0.14	0.05	0.07	0.06	0.12
ρ	0.95	0.88	0.88	0.88	
E_{SOMO}/kcal mol^{-1}	−2.15	−1.82	−1.82	−1.81	

Note. E is the total energy; E_{rel} is the relative energy of the comparatively most stable radical R_2; μ is the dipole moment; ρ is the spin population of the C(3), C(4), and C(5) atoms calculated according to Löwdin; and E_{SOMO} is the energy of SOMO.

However, the results of studying the behavior of the analogs of the R_1 radical upon mechanical decomposition,[16–18] photolysis,[20] and radiolysis of alkyl halides[21] do not favor this mechanism of FV transfer in the irradiated n-heptane.

The calculation of the electronic structure of the n-heptane molecule in the excited state showed that when the energy is absorbed, the excitation is mainly localized on the central C(3), C(4), and C(5) atoms. Our experiments indicate that the radiation yield of the radicals is independent of the irradiation dose. Therefore, we may assume the intramolecular transfer of the excitation energy from the end atoms to the central atom during radiolysis. On the other hand, the excitation transfer is accompanied by the radical formation, and the rates of these processes are comparable. Therefore, the indicated energy transfer from the end to central atoms "stops" precisely on the C(2) atom. A similar assumption that the selective radical formation during irradiation of polycrystalline and amorphous isobutane is due precisely to the distinctions in the primary processes rather than the isomerization of one type of radicals to another has been advanced previously.[22]

Thus, first, the selectivity of radical formation is due to the intramolecular transfer of the excitation energy from the end to central atoms; second, the intermolecu-

lar interaction has no effect on the radical formation during irradiation of the *n*-heptane polycrystals; third, the PM3 method well reproduces the experimental data on the structure of molecules and radicals of *n*-alkanes and is appropriate for calculations of the physicochemical properties of more complex (in composition and structure) molecular and radical systems.

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