Free Radical Formation in Hydrocarbon Crystals by γ Irradiation. II.[1]

Relative Yields of Isomeric Alkyl by Electron Spin Resonance

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Single crystals of the lower n-paraffins containing 4–16 carbon atoms give rise to esr spectra from secondary alkyl $CH_3\dot{C}HCH_2R$ (I) and $R'CH_2\dot{C}HCH_2R''$ (II) after γ irradiation at 77 or 195 K. The conformation of radicals formed in butane differs somewhat from those trapped in the long-chain n-alkane crystals. The relative yields of I and II were estimated by a least-squares fit. The predominant formation of I is shown to be inconsistent with estimates based on the analysis of final products. Possible explanations are discussed in terms of reactions along the particle tracks, and ionic mechanisms. A neutralization process is suggested which would lead to the preferential formation of radicals of type I by reason of the charge distribution in the positive radical ion primarily formed.

Introduction

Radiation chemical processes in liquid hydrocarbons[2] have been extensively investigated using chemical methods. The specific considerations relating to the peculiarities of the solid state have so far received less attention.[3] Only in a few cases has the radical yield following irradiation at 77 K of n-alkanes been determined.[4,5] These studies were based on an analysis of the final product distribution as shown by gas chromatography. This method involves several assumptions which are implicit in the analysis.[4] For this reason, a more direct estimate of the relative yields of free alkyl in the solid by means of esr was thought to be a valuable complement to the above studies.

Esr studies of irradiated single crystals allowed an unambiguous assignment of the radicals formed in several alkanes.[1] In this study the relative importance of different alkyl radicals has been estimated for hydrocarbons in the n-alkane series ranging from butane to hexadecane. A comparison of the yields in samples irradiated at temperatures of 77 K and 195 K has also been carried out, in order to find out whether the rigidity of the matrix has any influence on the nature and yields of the products.

The crystal structures of the lower n-paraffins[6] with an even number of carbon atoms are known to consist of one molecule in a triclinic unit cell. No data on butane are known, but the results obtained here indicate a higher symmetry. Of the odd-numbered alkanes, undecane was selected for investigation in order to determine whether the differences caused by an orthorhombic crystal structure[7] might affect the nature and yields of the free radicals formed.

Experimental Section

Single crystals of the hydrocarbons butane, hexane, octane, decane, undecane, and hexadecane were prepared according to a technique which has been previously described.[8] The crystals were irradiated using a ^{60}Co γ source and a dose rate of 0.7 Mrad/hr. All the samples received equal doses of approximately 2.5 Mrads. The irradiation temperature was either 77 K or 195 K.

Esr spectra were recorded at 77 K with a Varian E-9 spectrometer operating at a frequency of 9.15 GHz and a microwave power of 1 mW. The crystalline samples were contained in Suprasil tubes and could be rotated about the tube axis, at right angles to the magnetic field direction. In some cases a small piece of the tube was cut off in the cold. This piece could be rotated about an axis perpendicular to the tube axis by means of a quartz rod which had been fused to the Suprasil ampoule. This technique was also extended to allow for rotation about three mutually perpendicular axes. Three different pieces of the tube containing the crystal were then used, one for each axis of rotation.

Spectra intended for computer analysis were recorded in digital form on paper tape by means of a C-1024 time-averaging computer supplemented with a

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(1) Part I: T. Gillbro, P.-O. Kinell, and A. Lund, *J. Phys. Chem.*, **73**, 4167 (1969).

(2) T. Gäumann and J. Hoigné, Ed., "Aspects of Hydrocarbon Radiolysis," Academic Press, London, 1968.

(3) L. Kevan and W. F. Libby, "Advances in Photochemistry," Vol. II, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., New York, N. Y., 1964, p 183 ff.

(4) H. Widmer and T. Gäumann, *Helv. Chim. Acta*, **46**, 944 (1963).

(5) Ç. Bienfait, J. Ceulemans, and P. Claes, *Advan. Chem. Ser.*, **No. 82**, 300 (1968).

(6) (a) N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1747 (1961); (b) *ibid.*, **15**, 1755 (1961); (c) *ibid.*, **18**, 353 (1964).

(7) N. Norman and H. Mathisen, Central Institute for Industrial Research, Final Technical Report, Publication No. 334, Blindern, Oslo, 1961.

(8) T. Dahlgren, T. Gillbro, G. Nilsson, and A. Lund, *J. Sci. Instrum.*, **4**, 61 (1971).

TMC Model 220 data output unit and a Tally Model 420 tape perforator connected to the spectrometer.

The analysis of spectra containing several superimposed components was attempted using a computer-assisted method. The spectrum to be analyzed was fitted to an equation of the type

$$F(x_i) = \sum_{j=1}^{m} c_j f_j(x_i)$$

by a least-squares procedure using a number of equidistant field points x_i. Here c_j represents the fraction of the component f_j present. These components are simulated in the program[9] which employs the appropriate parameters for the coupling constants a, derivative line widths ΔH_{pp}, and g factors. Either Lorentzian (L) or Gaussian (G) derivative line profiles can be used.

Results

Butane. Only one component could be identified in the spectra obtained when the crystal was rotated about the tube axis. The spectrum shown in Figure 1a was obtained for a specific angle of rotation at which the line profile became almost symmetric with respect to its center. This line shape can be reasonably well simulated using the parameters given in Figure 1b. The slight asymmetry noted in Figure 1a which becomes pronounced for other angles of rotation is probably due to a site-splitting associated with the presence of several molecules in the unit cell.

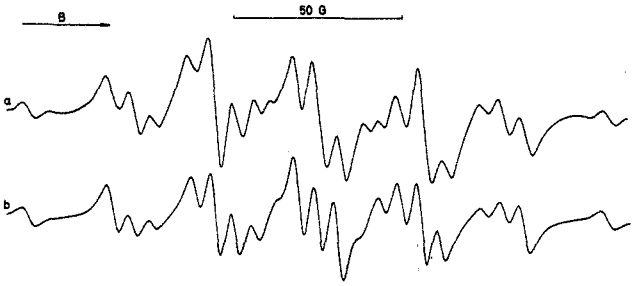

Figure 1. Esr spectrum from γ-irradiated butane at 77 K for a crystal orientation at which site-splitting caused minor asymmetry; (b) is a calculated spectrum for $CH_3\dot{C}HCH_2CH_3$ with $a_{CH_3} = 24.8$ G, $a_\alpha = 30.5$ G, $a_{\beta_1} = 36.4$ G, $a_{\beta_2} = 30.5$ G, $\Delta H_{pp} = 4$ G (L).

Hexane, Octane, Decane, and Undecane. The spectra obtained after irradiation at 77 K have been described previously.[1] With octane and decane a considerable improvement in spectral resolution was achieved when the sample was irradiated at 195 K. The spectrum shown in Figure 2a appeared when the field vector was adjusted for a maximum total splitting by rotating the decane crystal about the tube axis. The two components included in the fitting procedure are given in Figure 2b and Figure 2c, respectively, while the fit itself is reproduced in Figure 2d. The spectrum remaining after subtracting the component in Figure 2b from the experimental line profile is shown in Figure 2e.

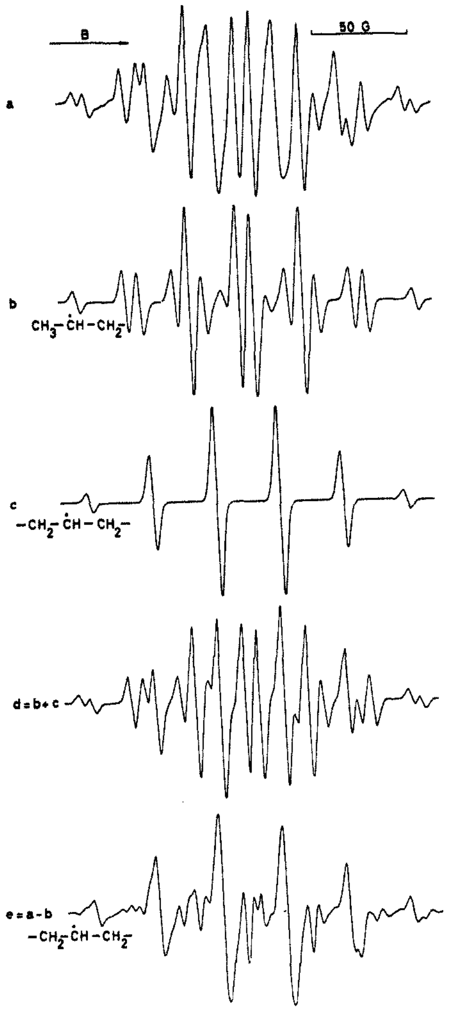

Figure 2. (a) Esr spectrum from a single crystal of decane γ-irradiated at 195 K and oriented to give a maximum overall separation; (b) simulated spectrum from $CH_3\dot{C}H(CH_2)_7CH_3$; (c) simulated spectrum from $-CH_2\dot{C}HCH_2-$; (d) spectrum synthetized from (b) + (c) through a least-squares fit to (a); parameters are given in Table I; (e) difference spectrum obtained from (a) − (b).

Spectra from an undecane sample irradiated at 195 K were less well resolved than those obtained from the hydrocarbons with an even number of carbon atoms under similar conditions. No quantitative analysis of these spectra has been carried through.

Hexadecane. The spectra from hexadecane irradiated at 77 K showed an anisotropy comparable to that obtained for the hexane, octane, and decane samples when the crystal was rotated about the tube axis, although the spectra exhibited a lower degree of resolution. The spectrum showing the maximum overall width, Figure 3a, could be analyzed in the same manner as the corresponding spectra for hexane, octane, and decane. This does not apply to the spectra obtained after irradiation of the crystal at 195 K, Figure 3b.

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(9) Program ASESK written by T. Vänngård (1961); revised and extended by A. Lund and T. Shiga (1971).

Table I: Relative Amounts of Isomeric Alkyl after γ Irradiation to 2.5 Mrads at 77 and 195 K. (The Resonance Parameters Are Those Employed in the Least-Squares Fit)

Hydrocarbon	T, K	Radical	a_{CH_3}, G	a_{CH_2}, G	a_α, G	ΔH_{pp}, G	Relative amount, %
Hexane	77	$CH_3\dot{C}H(CH_2)_3CH_3$	25.9	33.6	33.2	5(*L*)	85 ± 5[a]
		$CH_3CH_2\dot{C}H(CH_2)_2CH_3$		33.6	33.2	5(*L*)	15
Octane	77	$CH_3\dot{C}H(CH_2)_5CH_3$	25.0	33.0	32.0	5.5(*L*)	77
		$-CH_2\dot{C}HCH_2-$		33.0	32.0	5.5(*L*)	23
	195	$CH_3\dot{C}H(CH_2)_5CH_3$	25.0	33.0	33.0	4(*G*)	88
		$-CH_2\dot{C}HCH_2-$		33.0	33.0	4(*G*)	12
Decane	77	$CH_3\dot{C}H(CH_2)_7CH_3$	25.0	33.0	31.5	6(*L*)	73
		$-CH_2\dot{C}HCH_2-$		33.0	31.5	6(*L*)	27
	195	$CH_3\dot{C}H(CH_2)_7CH_3$	25.9	33.6	33.2	4(*G*)	63
		$-CH_2\dot{C}HCH_2-$		33.6	33.2	5(*G*)	37
Hexadecane	77	$CH_3\dot{C}H(CH_2)_{13}CH_3$	25.9	33.6	33.2	5.0(*L*)	54
		$-CH_2\dot{C}HCH_2-$				6.5(*L*)	46
	195	$CH_3\dot{C}H(CH_2)_{13}CH_3$	25.5	32.9	32.5	3.5(*G*)	59
		$CH_3\dot{C}H(CH_2)_{13}CH_3$	23.1	32.7	12.5	3.5(*G*)	
		$-CH_2\dot{C}HCH_2-$		32.9	32.5	3.5(*G*)	41
		$-CH_2\dot{C}HCH_2-$		32.7	12.5	3.5(*G*)	

[a] The error quoted is the maximum deviation in a series of five independent determinations employing either different samples or differently oriented samples.

A site-splitting is indicated by the fact that two maxima of the overall total width were found at about right angles to each other when the crystal was rotated about the tube axis. The spectrum of Figure 3b was accordingly considered to comprise four components, two from each of two sites. Each site contributes equally to the signal strength since they represent chemically equivalent molecules within the unit cell. The resulting fit (see Figure 3c) was obtained from the input data of Table I.

Discussion

An account of the radical structure formed in the crystalline *n*-alkanes after γ irradiation at 77 K has previously been presented.[1] Similar species are formed after irradiation at 195 K. As a result of the improved resolution in the latter case, the assignments can be made with an increased confidence. The analysis of the spectra from decane shows that the main component (I) is characterized by the approximately isotropic couplings $a_1 = 25 \pm 1$ G (3H) and $a_2 = 33 \pm 1$ G (2H) and an anisotropic coupling a_3 (1H) which is typical of the

$$CH_3\dot{C}HCH_2R$$
$$\text{I}$$

type of radical. This species also predominates after γ irradiation at 77 K.[1]

The subtraction of the absorption due to I reveals the presence of a second component in the spectrum shown in Figure 2a. In addition to the spurious peaks attributed to the imperfection of the subtraction procedure, component II in Figure 2e comprises six lines with an approximately binominal intensity distribution. This could arise from a radical of the type

$$RCH_2\dot{C}HCH_2R'$$
$$\text{II}$$

where $a_{CH_2} \approx a_\alpha = 33$ G.

The narrower line width obtained at the higher temperature supports the hypothesis that the main broadening mechanism is the dipole–dipole interaction[5] between radicals formed in close proximity. At 195 K the matrix is softer, and this permits the recombination or diffusion of radicals formed close to the track of the ionizing particle.

In all cases except for butane, rotation about the tube axis yielded essentially similar spectra for the crystals; this indicates that there is a preferential crystal growth along this axis. Crystallographic data for pentane[6c] show that the mode of packing is quite distinct from those of the other *n*-paraffin structures. The chain axes of the pentane molecules in the unit cell are not parallel to each other. The site-splitting observed in butane indicates that the same phenomenon occurs here also. The nonequivalence of the methylene proton interactions (Figure 1) is attributed to the perturbing influence of the neighboring end methyl group.

With the exception of butane, there is little difference in the conclusions which can be drawn about radical structure in the other hydrocarbons. This should be particularly noted for the undecane crystal. In early studies of esr spectra of powdered hydrocarbons,[10] narrow lines were observed for the odd-numbered alkanes, but this feature could not be produced for the single crystal. Thus, the difference in crystal struc-

(10) A. V. Topchiev, Ed., "Radiolysis of Hydrocarbons," Elsevier, Amsterdam, 1964, Chapter III.

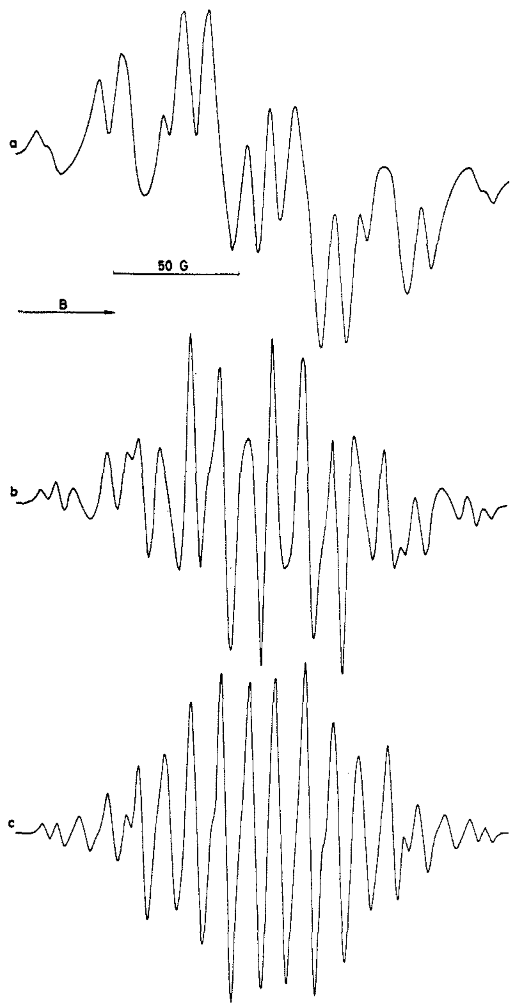

Figure 3. Esr spectra from a single crystal of hexadecane at 77 K oriented as described in Figure 2: (a) γ-irradiated at 77 K; (b) γ-irradiated at 195 K; (c) spectrum composed of the absorptions from $CH_3\dot{C}H(CH_2)_{13}$ CH_3 and $-CH_2\dot{C}HCH_2-$, each radical occupying two sites. Parameters are given in Table I.

ture[7] which exists between this hydrocarbon and decane has no noticeable effect upon free radical formation.

Yields. Free radical processes in the radiation chemistry of *n*-alkanes have previously been investigated in the liquid state by the analysis of final products.[4,10] The yields of the three isomeric hexyl radicals as estimated from the product distribution after irradiation at −78°[4] were in the ratio 35:39:26 for 3-hexyl, 2-hexyl, and 1-hexyl, while at 50° the ratio found was 41:50:9. After irradiation of the solid at −196° the following yields of C_{12} products were reported:[4] $G_{3,3} = 0.10$ (4,5-diethyloctane), $G_{2,3} = 0.24$ (4-ethyl-5-methylnonane), $G_{2,2} = 0.17$ (5,6-dimethyldecane), $G_{1,3} = 0.16$ (4-ethyldecane), $G_{1,2} = 0.20$ (5-methylundecane) and $G_{1,1} = 0.08$ (dodecane). The relative importance of the three radicals should then be given by the ratio $G_1:G_2:G_3 = (2G_{1,1} + G_{1,2} + G_{1,3}):(G_{1,2} + 2G_{2,2} + G_{2,3}):(G_{1,3} + G_{2,3} + 2G_{3,3}) = 27:41:32$.

The disagreement with the data obtained in this study is obviously a result of the different methods used to estimate the yields. The initial distrubution may deviate from that measured by esr unless the following conditions prevail: (1) no recombination of radicals may occur prior to the recording of the spectra; (2) the transformation of one type of radical into the other must be negligible; and (3) the validity of the least-squares data analysis must be established.

The violation of the first point would lead to erroneous conclusions if, for example, 1-hexyl radicals react with each other to form dodecane. In the crystal the distance between the terminal CH_3 groups of two adjacent molecules is only 3.62 A. Radical pairs are known to be formed in the solid,[11] probably as a consequence of the heterogenous distribution of energy by the ionizing radiation. Because of the short intermolecular distance, two 1-hexyl radicals formed in a track might be able to recombine even in the solid state. In a similar way other products might be formed at low temperatures by the reaction of radicals created in close proximity to each other.

Postirradiation reactions have been observed by esr in alkyl halide matrices[12] in which *n*-alkyl changed into *sec*-alkyl at 77 K. However, the reaction is slow because of its relatively high activation energy. This second point may therefore be of less importance.

The method of estimating the relative importance of each radical requires that the spectra of the components be known. The deliberate selection of a coupling constant which was too large by 10% for one of the components altered the estimates of the relative strength by about 5%. A rather large displacement of the center from its correct position, by one third of a line width, caused an error of 20%. It is not claimed that the resonance parameters of Table I are the optimal ones for minimizing the standard deviation of the fit. In order to achieve this condition, it would have been necessary to employ an automatic adjustment procedure for these parameters. However, five independent estimates indicated that the relative amounts of isomers in hexane could be reasonably well reproduced (Table I). Although these test runs indicate that considerable errors may arise, they would not in themselves be sufficient to account for the difference in results obtained by the analysis of final products.

The estimate of radical yields from the distribution of dimer products is an indirect method and is therefore sensitive to the reaction mechanism. The assumptions which are made here and the justification for these have been discussed by Widmer and Gäumann.[4] For reasons mentioned above, the hypothesis that radical recombination is independent of concentration,

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(11) M. Iwasaki, T. Ichikawa, and T. Ohmori, *J. Chem. Phys.*, **50**, 1991 (1969).

(12) P. B. Ayscough and C. Thomson, *Trans. Faraday Soc.*, **58**, 1477 (1962).

which in particular means no track effect, may be invalid as far as solid state radiolysis is concerned. In this case where diffusion is slow, dimers should form preferably by recombination between radicals formed in close proximity to each other. Geometrical factors determined by the crystal structure would then have a selective effect upon the ability of the isomers to react. Thus the rule of statistical combination, which is valid in the liquid,[4] may be violated. Another severe restriction in this analysis is the neglect of ionic processes. The results of the radiolysis of pentane[5] have indicated that ion-molecule reactions may contribute to some extent to dimer formation in the solid state, and even more so in the case of trimers. An entirely ionic mechanism has been proposed to explain the formation of hexenes and dimers in the solid state radiolysis of hexane.[3] In this theory the formation of uncharged radicals is attributed to cases of bond disruption on neutralization of an ion radical formed primarily. The abstraction of hydrogen by the ion radical followed by neutralization and molecular hydrogen ejection creates a radical pair. About 10% of the radicals are trapped in pairs in the case of *n*-hydrocarbons.[11] The amount originally formed is difficult to estimate due to the recombination which might occur even at 77 K.

A molecular orbital calculation involving all valence electrons at the INDO level of approximation[13] yields the following charges on the carbon atoms of the hexane cation: $q_1 = 0.035$, $q_2 = 0.093$, $q_3 = 0.079$. The neutralization process should preferably occur at the carbon atom carrying the largest proportion of the positive charge. The energy gained in this reaction would be localized and could be used in C–H bond scission. The dominant formation of 2-hexyl is then qualitatively explained.

Conclusions

The relative yields of isomeric radicals determined by esr measurements do not conform with estimates from the final product distributions. Ionic mechanisms and/or reactions taking place within the track of the ionizing radiation in the solid may explain the discrepancy. Radicals of the type $CH_3\dot{C}HCH_2R$ are most easily trapped possibly as a consequence of their formation from the ion radicals. Irradiation at 195 K as opposed to 77 K gives a negligible effect upon the relative yields but influences the ability of the matrix to trap intermediates close to each other, *i.e.*, along the track of an ionizing particle.

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(13) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).