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Abstract

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On the Formation of Free Radicals and Atoms during the Radiolysis of Hydrocarbons at a Temperature of 77 °K

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The literature contains indications that, under the action of ionizing radiation (X-rays, γ-rays, fast electrons, etc.) on hydrocarbons, free radicals are formed as a result of the rupture of C–C or C–H bonds (^1). In the radiolysis of liquid hydrocarbons the lifetime of the radicals is very short, their stationary concentrations are small, and their formation can presumably be judged only from the composition of the final products. Thus, for example (^2), under irradiation of liquid heptane (Co^60 source of the L. Ya. Karpov Physico-Chemical Institute), the degree of conversion increases linearly with increasing dose, reaching 10% at a dose of $3 \cdot 10^8$ r.

As the principal products of radiolysis, along with liquid products with one and two conjugated double bonds, H_2 and $C_{14}H_{30}$ are formed; the latter may be regarded as a dimer of the heptyl radical, assuming atomic hydrogen and the radical C_7H_{15} to be the primary products of heptane dissociation. To provide direct proof of this assumption, heptane was irradiated at low temperature in the frozen state; under these conditions, because of the low mobility of the radicals and atoms formed under the action of γ-quanta, their recombination is hindered, and it could be expected that appreciable concentrations of free radicals frozen in this way could be accumulated. Irradiation of heptane, as well as of other hydrocarbons, in the solid frozen state was carried out in the apparatus mentioned above. A weighed portion of pure hydrocarbon in a carefully evacuated sealed quartz ampoule ($d = 2$–4 mm) was placed at the bottom of a tall glass Dewar vessel filled to the top with liquid nitrogen. As the liquid nitrogen evaporated, more was added to the vessel so that the ampoules remained below the nitrogen level at all times. Under these conditions, the yield of tetradecane proved to be approximately 2 times smaller than in heptane irradiated in the liquid state.

For the detection of radicals, their identification, and measurement of their concentration, the irradiated samples were transferred without thawing into a special Dewar vessel made of foam plastic, placed in the resonator of an electron paramagnetic resonance (EPR) spectrometer. We used two EPR instruments.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

To establish the presence of radicals and to determine the character of the hyperfine structure of the corresponding EPR spectra of the hydrocarbons studied, an instrument with high-frequency modulation of the magnetic field was used, making it possible to photograph on the screen of an electronic oscilloscope the first derivative of the spectrum. The sensitivity of this instrument, operating at a wavelength of ~3 cm, was approximately $4 \cdot 10^{-10}$ moles of diphenylpicrylhydrazyl. Measurement of the splitting of the hyperfine structure of the spectrum was carried out with a nuclear magnetic-field meter. Estimation of the concentration of free radicals in the samples studied

was carried out by comparing the integral intensity of the EPR signal on an ordinary video spectrometer with the corresponding value for a given amount of the paramagnetic salt $CuSO_4 \cdot 5H_2O$.

Fig. 1. Spectra of electron paramagnetic resonance of alkyl radicals arising under γ-irradiation: hexane (a), heptane (b), and cetane (c)

The following hydrocarbons were studied: hexane, heptane, octane, dodecane, cetane, isooctane, cyclohexane, benzene, and toluene. In all cases intense EPR signals with a g-factor close to 2.0 were observed. In the case of paraffinic hydrocarbons and cyclohexane, a quite distinct pattern of hyperfine splitting was observed, as a result of which the total line width amounts to from 100 to 170 oersteds.

As can be seen from the photographs presented (Fig. 1), the character of the hyperfine structure changes substantially with changes in the structural characteristics of the original molecule. Spectra of an analogous type were observed by Gordy and McCormick (3) upon irradiation with X-rays of dimethyl- and diethylmercury, diethylzinc, etc., and were attributed by these authors to alkyl radicals. Spectra of this kind, obtained upon irradiation of hydrocarbons, have not yet been reported in the literature.

Fig. 2. Doublet component of the spectrum of the hydrogen atom (1) and spectrum of an alkyl radical (2)

Another feature of the EPR spectra of the hydrocarbons irradiated by us in the frozen state is the presence in them of appreciable concentrations of hydrogen atoms, as indicated by two narrow signals symmetrically located approximately 250 oersteds on either side of the signal of the alkyl radical (see Fig. 2). Hydrogen atoms were observed (4) upon irradiation by γ-rays of solid acids frozen at 77° (phosphoric, sulfuric, and hydrochloric); however, it was difficult to suppose that their lifetime under our conditions would prove sufficient for appreciable concentrations to be preserved for any considerable length of time. Repeated measurements over the course of two weeks showed,

that both alkyl radicals and hydrogen atoms are sufficiently stable at the temperature of liquid nitrogen. It was also established by direct experiments that, after removal of the liquid nitrogen, the concentration of hydrogen atoms begins to decrease only after 10–12 sec, and the concentration of radicals after 30–35 sec. It follows from this that, during the operation of transferring ampoules from one Dewar vessel to another (when placing them in the resonator), no appreciable change in the concentrations of the active particles occurs.

On the other hand, on this basis one may suppose that hydrogen atoms are stabilized not in the bulk of the frozen hydrocarbons, but on the inner surface of the quartz ampoule. The possibility of such stabilization of hydrogen atoms during irradiation of ice is also indicated in work (4).

A detailed analysis of the obtained EPR spectra of free radicals is not within the scope of the present article. It is necessary, however, to make several qualitative remarks. First of all, the very fact of the presence of hyperfine structure and the anomalously large magnitude of the splitting (of the order of 25 oersteds) attracts attention. According to Gordy (3), this indicates, first, the possibility of some displacements of H atoms in the radical with respect to the immobile carbon skeleton, which ensure the appearance of hyperfine structure, and, second, the presence of an appreciable density of the unpaired electron on the hydrogen atoms. The large number of components of the hyperfine structure (see Fig. 1) further shows that, apparently, not only hydrogen atoms directly bonded to the carbon atom carrying the free valence take part in the splitting, but also, at least, hydrogen atoms situated in the β-position. Comparison of the spectra of hexane, heptane, and ethane shows that, in the case of the first two compounds, the hyperfine structure consists of an odd number of components, and in the third, of an even number. Since in ethane the relative probability of bond rupture in the CH_2 group with respect to the CH_3 group is greater than in hexane and heptane, the splitting on the nearest hydrogen atom should lead precisely to an even pattern. The odd number of components in the case of *n*-hexane and *n*-heptane can apparently be regarded as an indication that, in these compounds, the CH bond in the CH_3 groups is preferentially ruptured.

The quantitative measurements carried out by us, using heptane as an example, of the concentration of free radicals at a dose of $\sim 10^7$ r have been compared in Table 1 with data from chemical analysis of a sample irradiated under completely identical conditions.

Table 1

Number of radicals	**Number of radicals**
According to paramagnetic-resonance data, per 1 g	According to calculation from the amount of radiolysis product obtained, per 1 g
$(4.9 \pm 1) \cdot 10^{18}$ $(7.1 \pm 1) \cdot 10^{18}$	$6.1 \cdot 10^{18} \pm 10\%$

Taking into account a possible small error in the dose (10–15%), the agreement of the results of the two measurements is quite satisfactory. The close agreement with the analytical data, on the one hand, confirms the correctness of the method for estimating concentrations, and, on the other, shows that, when approximately 0.1% of the molecules dissociate into radicals at the temperature of liquid nitrogen, these radicals practically do not enter into any secondary reactions.

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1. Collected volume, *Radiation Chemistry*, Foreign Literature Publishing House, 1953; Collected papers on radiation chemistry, Publishing House of the Academy of Sciences of the USSR, 1955; *Disc. Farad. Soc.* **12** (1952).
2. L. S. Polyak, A. V. Topchiev, N. Ya. Chernyak, DAN, **119**, No. 2 (1958).
3. W. Gordy, C. G. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956).
4. R. Livingston, H. Zeldes, E. H. Taylor, *Disc. Farad. Soc.*, **19**, 166 (1955).

Note: Figure translations are in progress. See original paper for figures.