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Abstract

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Radiolysis of Heptane and Some Other Alkanes

The present communication is the first in a planned series of works devoted to the study of the basic regularities and mechanism of the radiolysis of individual hydrocarbons of the paraffin series in the liquid and solid phases under the action of γ-radiation.

As the radiation source, γ-radiation from Co^{60} installations of nominal power 1400 and 20,000 Cu was used. The main work was carried out with *n*-heptane, but other individual hydrocarbons were also used. The purified hydrocarbons were completely transparent in ultraviolet light, and their specific gravities and refractive indices (with the exception of cetane) did not differ from those reported in the literature.

Irradiation of the hydrocarbons was carried out in sealed ampoules of molybdenum glass, the hydrocarbon first being carefully deoxygenated.

When ampoules containing a product that had received a definite radiation dose were opened, the amount of gas evolved was determined. The gas was then analyzed for its content of H_2, CH_4, and other hydrocarbon gases by chromatographic separation on carbon and silica gel. The accuracy of determining the total gas yield was \$±\$5%. In the liquid product, its specific gravity, refractive index, molecular weight (by the cryoscopic method), and iodine number (according to Margoshes) were determined. In addition, ultraviolet and infrared spectra of the irradiated products were recorded, and distillations and sulfonation were carried out.

A change in temperature in the interval from −30 to +200° does not affect the yield or the character of the gaseous radiolysis products. Special experiments showed that at the moment irradiation is stopped gas evolution ceases, and upon resumption of irradiation it proceeds in the same way as before the interruption.

Figure 1 gives curves characterizing the changes obtained as a result of irradiation in liquid heptane and the total yield of gas in dependence on the absorbed dose of γ-radiation. For doses within the range from 0 to $500 \cdot 10^6$ r, the dependences of the amount of gas formed in the radiolysis process, the increase in molecular weight, the specific gravity, and the refractive index of the liquid phase on dose are linear in character. The dependence of the iodine number of the liquid phase on dose is approximately linear up to a dose of $\sim 150 \cdot 10^6$ r, and then levels off, changing little over very wide dose intervals.

Fig. 1

Figure 1: Fig. 1

We have considered the question of the influence of the number of CH_2 groups and of the relative content of CH_3 groups in the molecule on the results of radiolysis (Table 1). The amount of methane increases as a function of the relative number of CH_3 groups in the hydrocarbon molecule, from 0 for cyclohexane to 37% for isooctane. The relative increase in density and refractive index of irradiated normal alkanes from C_6 to C_{12} increases linearly; the values of these increases for C_{16} not only do not fit this dependence, but also have a sharply reduced value.* All the data for isooctane are smaller than for *n*-octane.

* It is interesting to note that in work ([1]) it was shown that the yield of hydrogen for fatty acids (arachidic, behenic, melissic) increases linearly with an increase in the number of C atoms in the molecule up to acid C_{16}; thereafter it decreases.

The irradiated heptane was subjected to vacuum distillation at ~ 0.5 mm Hg, the first fraction being distilled off with ice cooling, and then distillation was continued at room temperature until the remaining heavy fraction reached constant weight. The fractions were frozen out in a trap cooled with liquid nitrogen. The lightest fraction in all cases had a molecular weight of ~ 100, and an iodine number, depending on the dose, of ~ 2–3. It contained light radiolysis products distilling together with heptane–heptene, heptadiene, and their analogues.

Fig. 1. 1 –gas yield in cm^3 (N.T.P.) per 1 cm^3 of initial *n*-heptane; 2 –change in molecular weight of the liquid; 3 –change in specific gravity of the liquid ($\Delta d_4^{20} \cdot 10^3$); 4 –change in refractive index of the liquid ($\Delta n_D^{20} \cdot 10^3$); 5 –iodine number of the liquid

Table 1

Hydrocarbon	Ratio $\frac{CH_3}{CH}$	Gas composition (methane-hydrogen fraction), %: H_2	Gas composition (methane-hydrogen fraction), %: CH_4	$\frac{\Delta d}{d_{orig}}$, %	$\frac{\Delta n}{n_{orig}}$, %
Cyclohexane	0	100	0	12.0	3.5
n-Cetane	0.059	98.5	1.5	7.8	2.7
n-Dodecane	0.077	–	–	11.5	5.8
n-Octane	0.111	97.5	2.5	10.1	3.6

Fig. 2

Figure 2: Fig. 2

Hydrocarbon	Ratio $\frac{CH_3}{CH}$	Gas composition (methane-hydrogen fraction), %: H_2	Gas composition (methane-hydrogen fraction), %: CH_4	$\frac{\Delta d}{d_{orig}}$, %	$\frac{\Delta n}{n_{orig}}$, %
n-Heptane	0.125	97.0	3.0	9.6	3.25
n-Hexane	0.143	96.8	3.2	8.4	3.1
Isooctane	0.278	63.0	37.0	8.8	2.8

at a constant dose of $250 \cdot 10^6$ *r*

From consideration of the curves in Fig. 2 it is evident that, with increasing dose, the weight percent of the heavy residue and its refractive index increase in proportion to the dose. The molecular weight of the heavy residue in the eight measurements made ranges from 175 to 218, averaging $\sim$ 200. The specific gravity of the heavy residue is 0.760–0.800.

At the beginning of radiolysis, at comparatively small doses, while the formation of polymers may practically be neglected, the elemental composition

the heavy residue coincides with the elemental composition of tetradecane. The percentage of carbon increases linearly with dose, and at doses of $\sim 400 \cdot 10^6$ r the elemental composition falls outside the limits of the homologous series of alkanes, owing to an increase in the amount of unsaturated compounds and their polymers. Sulfonation of the heavy residue was carried out. For a dose of $309 \cdot 10^6$ r it showed 19% unsaturated and 81% saturated compounds.

In addition to the above, the following experimental facts must also be taken into account: 1) in the liquid irradiation product there are trans-heptenes, as shown by the infrared spectra ([2]); 2) in the liquid irradiation product there are dienes (and polyenes), as shown by the ultraviolet absorption spectra ([2]).

Fig. 2. Change in the heavy residue in wt.% *(1)*, its refractive index *C (2)*, and elemental composition n_D^{20}, % *(3)* as a function of dose.

In work ([3]), with the aid of liquid chromatography, it was shown that in the radiolysis of hexane (at doses of the same order as those used by us) dimers, both saturated and unsaturated, are formed in considerable quantity.

On the basis of the experimental data presented above and of generally accepted ideas about the nature of the reactions ([4–9]) occurring under the action of ionizing radiation, the following possible initial reactions of heptane radiolysis may be outlined:

$$1 \quad \left.\begin{matrix} C_7H_{16}^+ + e \\ C_7H_{16}^+ + e \end{matrix}\right\} \rightarrow C_7H_{15} + H \qquad C_7H_{16} \rightsquigarrow C_7H_{16}^* \rightarrow C_7H_{15} + H^*$$

$$1' \quad H^* + RH \rightarrow H_2 + R\cdot, \qquad C_7H_{15} + C_7H_{15} \rightarrow C_{14}H_{30}, \qquad H + H \xrightarrow{+M} H_2.$$

$$2 \quad \left.\begin{matrix} C_7H_{16}^+ + e \\ C_7H_{16} + e \end{matrix}\right\} \rightarrow C_7H_{16}^* \rightarrow C_7H_{14} + H_2 \qquad 3 \quad C_7H_{16}^* \rightarrow C_7H_{12} + 2H_2$$

$$4 \quad \left.\begin{matrix} C_7H_{16} + e \\ C_7H_{16}^+ + e \end{matrix}\right\} \rightarrow C_6H_{13} + CH_3; \qquad 4' \quad CH_3 + RH \rightarrow CH_4 + R\cdot$$

$$C_6H_{13} + RH \rightarrow C_6H_{14} + R\cdot$$

$$5 \quad C_7H_{16}^* + C_7H_{16}^* \rightarrow C_{14}H_{30} + H_2. \qquad C_7H_{16}^* + C_7H_{16} \rightarrow C_7H_{15} + C_7H_{15} + H_2 \rightarrow C_{14}H_{30} + H_2$$

Reaction 4, judging from the amount of methane in the gas, is considerably less probable than the reactions leading to the formation of hydrogen.

Our detection, by means of the paramagnetic-resonance spectrum, of the heptyl radical and atomic hydrogen in irradiated frozen heptane proves that reaction 5, even if it does occur, in any case does not play the principal role.

Further development of the process proceeds in the following way. Interaction of the radical C_7H_{15} with a molecule of the initial hydrocarbon will not lead to the formation of any new radical or molecular product; therefore, for its further transformation, the most probable process is recombination of two C_7H_{15} radicals with formation of tetradecane (1′). Recombination of the radical C_7H_{15} and the radical C_6H_{13}, formed according to reaction 4, is less probable, since the amount of C_6H_{13} is small in comparison with the amount of C_7H_{15}. For the same reason, formation of dodecane by recombination of C_6H_{13} radicals is improbable (the radical C_6H_{13} is more likely to give a molecule of hexane upon interaction with a molecule of the initial hydrocarbon (4′)). The secondary

Fig. 3. Paramagnetic-resonance spectrum: a—heptyl radical; b—heptyl radical and atomic hydrogen

Figure 3: Fig. 3. Paramagnetic-resonance spectrum: a—heptyl radical; b—heptyl radical and atomic hydrogen

reactions taking place are polymerization reactions of the conjugated dienes obtained by reaction 3.

Since, for any possible variant of the reaction leading to the formation of hydrogen molecules in the gas phase, the sum of the unsaturated and saturated molecules (heptane dimer) in the liquid phase must be equal to the number of hydrogen molecules, then for small doses (so long as polymerization of the unsaturated compounds can be neglected) the balance can be reduced. We have: hydrogen yield 4.5 ($±$10%), yield of unsaturated compounds 1.5, saturated compounds 2.5 molecules per 100 eV.

Thus, saturated + unsaturated compounds are less than hydrogen by ~11%, which lies within the accuracy of the measurements.

Fig. 3. Paramagnetic-resonance spectrum: *a*—heptyl radical; *b*—heptyl radical and atomic hydrogen

To confirm the existence of a free-radical pathway in the complex of radiolysis reactions, it was necessary to obtain direct proof of the formation of free radicals during radiolysis. Such proof was obtained by us by stabilizing radicals at low temperature. Heptane was irradiated in the frozen state at 77°K (in liquid nitrogen). Then, while it was kept at this temperature, the paramagnetic-resonance spectrum was recorded. The spectrum was recorded at the Institute of Chemical Physics of the Academy of Sciences of the USSR on the apparatus of Prof. V. V. Voevodskii, to whom we express our deep gratitude. A spectrum possessing a characteristic fine structure was obtained. It showed the presence in the irradiated frozen heptane of free alkyl radicals, and also, although in smaller quantity, free hydrogen atoms (Fig. 3). Upon thawing the irradiated heptane, recombination of radicals occurs, which we clearly followed from the gradual disappearance of the paramagnetic-resonance spectrum.

Thus, in addition to evidence for the free-radical pathway of some reactions in the radiolysis of alkanes, it was shown that alkyl radicals can be accumulated upon irradiation of hydrocarbons in the frozen state at a temperature of 77°K, and that even hydrogen atoms are partially preserved at this temperature for a very long time, which opens new possibilities for the chemistry of hydrocarbons.

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CITED LITERATURE

1. V. Whitehead, K. Gumen, I. Breger, *Collection: Radiation Chemistry*, Izd. inostr. lit., 1953, p. 286.

2. L. S. Polak, A. V. Topchiev, N. Ya. Chepnyak, I. Ya. Kakurova, *DAN*, **119**, No. 1 (1957).

3. H. A. Dewhurst, E. H. Winslow, *J. Chem. Phys.*, **26**, No. 4, 969 (1957).

4. S. Ya. Pshezhetskii, M. T. Dmitriev, *Uspekhi khimii*, **26**, issue 7, 725 (1957).

5. F. W. Spiers, *Disc. Farad. Soc.*, No. 12, 13 (1952).

6. F. S. Dainton, *Ann. Rev. Nucl. Sci.*, **5**, 213 (1955).

7. D. J. Magi, M. Barton, *Collection: Radiation Chemistry*, Izd. inostr. lit., 1953, p. 18.

8. A. Prevost-Bernas, A. Chapiro et al., *Disc. Farad. Soc.*, No. 12, 98 (1952).

9. M. H. J. Wijnen, *J. Chem. Phys.*, **24**, 851 (1956).

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