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Abstract

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RADIOLYSIS OF *n*-HEXANE IN THE REGION OF SMALL INTEGRAL DOSES
($3 \cdot 10^{18}$—$1 \cdot 10^{20}$ eV/ml)

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The study of the radiolysis of *n*-hexane at temperatures of 15–25° is of considerable interest for elucidating the features of the radiolysis of liquid *n*-alkanes. For this reason, the radiolysis of *n*-hexane has been studied in considerable detail (see, for example, ([1–4])). However, in all works known to us on the radiolysis of paraffin hydrocarbons, the kinetics of accumulation and the composition of the products were studied at doses not less than 0.5—$1 \cdot 10^{21}$ eV/ml, in a region that is certainly nonlinear ([5]).

In the present work, the yield of hydrocarbon products of the radiolysis of *n*-hexane C_1—C_4 was studied in the region of substantially smaller integral doses, 3—$100 \cdot 10^{18}$ eV/ml, at a constant dose rate of $6.60 \cdot 10^{14}$ eV/ml • sec. A Co-60 installation was used as the source of γ-radiation. Irradiation of previously degassed samples of pure *n*-hexane (volume 0.2–0.3 ml) was carried out in sealed small glass ampoules (ampoule volume 0.4–0.5 ml) at room temperature.

Commercial *n*-hexane used for filling the ampoules was treated with sulfuric acid and oleum, purified on a column with ASM silica gel, and distilled at atmospheric pressure. The absence of aromatic and diene hydrocarbons was checked from absorption spectra in the ultraviolet region; the purity of the *n*-hexane was also checked by chromatographic and mass-spectrometric methods.

The gaseous products of the radiolysis of *n*-hexane C_1—C_4 were analyzed by gas chromatography. The chromatographic column, 75 × 0.6 cm, was packed with ASK silica gel, onto the surface of which KOH (2 wt.%) had previously been deposited. Samples of irradiated hexane were analyzed on the chromatographic column at room temperature; the flow rate of the carrier gas (hydrogen) was 40 ml/min. To avoid losses of gaseous radiolysis products, introduction of the sample into the column was carried out by breaking the irradiated ampoule with the aid of a specially designed device ([6]).

As detector, use was made not of a katharometer, whose sensitivity for analysis of the products of hexane radiolysis formed in the region of small integral doses is clearly insufficient, but of a highly sensitive flame-ionization detector ([7]), the design* of which is shown in Fig. 1. To amplify the weak ion currents of the hydrogen flame, a "Kaktus" microammeter was used; chromatograms were recorded with a self-recording potentiometer of the EPP-09 type (10 mV scale, carriage travel time 2.5 sec). The use of a flame-ionization detector makes it possible to analyze impurities whose content in the main product does not exceed 10^{-5} wt.%. The sensitivity of this detector for propane was not less than $2 \cdot 10^{-10}$ mole (input resistance 10 GΩ). The detector and the sample-introduction device were thermostatted at 60°. The amount analyzed gaseous products was determined by the method of absolute calibration. The calibration constant was determined with an accuracy of $±$5%.

Table 1 gives averaged data on the yield of gaseous radiolysis products in milliliters of gas per 1 ml of liquid *n*-hexane at various integral irradiation doses. To characterize the convergence of the results, the results of analyses of individual ampoules are given for the dose $29.4 \cdot 10^{18}$ eV/ml. Deviations from the mean value do not exceed $±$10% rel.

Fig. 1. Flame-ionization detector. 1 —rod of the central inlet, 2 —nut for adjusting the distance between the nozzle and the electrode, 3 —base, 4 —insulating bushing (Teflon), 5 —nozzle (stainless steel), 6 —nozzle-current lead connector, 7 —cup, 8, 13 —grid, 9, 10 —stop screws, 11 —measuring-electrode connector, 12 —tee

Figure 2 presents, in logarithmic coordinates, the dependence of the total yield of several gaseous radiolysis products on the integral dose. Representing the experimental data in logarithmic coordinates makes it possible to reveal more clearly the character of the dependence of the yield of gaseous products on the magnitude of the dose. As is seen from Fig. 2,

$$\lg P = \lg k + \lg D, \text{ i.e. } P = kD^a,$$

where $a_{C_1-C_4} = 0.92$, $a_{C_2-C_4}$ (alkanes) $= 0.92$; $a_{C_2-C_4}$ (olefins) $= 0.88$. Thus, in the investigated region of small integral doses, the yield of gaseous radiolysis products tends to deviate from a linear dependence.

Table 1

Yield of gaseous products in γ-radiolysis of *n*-hexane

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* The design was developed jointly with engineer S. K. Krasheninnikov of the Special Design Bureau, INKhS.

Radiolysis product	Integral dose, eV/ml: $3.0 \cdot 10^{18}$		Integral dose, eV/ml: $11.5 \cdot 10^{18}$		Integral dose, eV/ml: $19.5 \cdot 10^{18}$, analysis of individual ampoules				Integral dose, eV/ml: $19.5 \cdot 10^{18}$, average		Integral dose, eV/ml: $100 \cdot 10^{18}$	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Methane	0.66	10.8	2.21	10.6	4.47	4.06	4.53	4.80	4.65	10.8	16.7	11.6
Ethane	1.25	20.4	4.03	19.3	9.28	9.50	9.53	9.00	9.33	21.6	33.7	23.4
Ethylene	1.10	18.1	3.24	15.6	6.82	7.53	8.45	7.66	7.62	17.7	23.2	16.2
Propane	1.30	21.2	4.00	19.2	8.05	7.90	7.80	8.50	8.06	18.7	28.0	19.4
Propylene	0.35	5.7	1.71	8.2	3.50	3.06	3.70	3.40	3.41	7.9	9.9	6.9
Butane	1.05	17.2	4.30	20.6	7.62	7.45	6.75	7.45	7.32	17.0	26.9	18.7
Butene-1	0.40	6.6	1.35	6.5	2.98	2.56	2.34	2.76	2.66	6.3	5.5	3.8
Total	6.11	100.0	20.84	100.0	42.72	42.06	43.10	42.57	43.05	100.0	143.9	100.0

Note. *a*—gas yield in ml $\cdot 10^3$ per 1 ml of C_6H_{14}; *b*—the same, in mole percent.

It must be noted that, in the studied interval of integral irradiation doses, apparently there occurs a reaction of hydrogenation of unsaturated compounds by thermal hydrogen atoms (it is assumed that the reactions proceed not in tracks, but in the bulk).

In some works (8) this reaction is not taken into account, while the predominant reaction is considered to be the abstraction of a hydrogen atom from an alkane molecule:

$$\dot{H} + C_6H_{14} \rightarrow H_2 + C_6H_{13}^{\cdot} \tag{1}$$

It can be shown, on the basis of the values of the corresponding rate constants, correspond-

···of the reactions proceeding in the gas phase (^{9}), that even in the region of small doses, when the total concentration of unsaturated products is still very small, the predominant reaction is the hydrogenation of the unsaturated compounds:

$$\mathrm{H}\cdot + M(C=C) \rightarrow MH\cdot. \tag{2}$$

Indeed,

$$\frac{k_1[\mathrm{C_6H_{14}}]\cdot[\mathrm{H}\cdot]}{k_2[M(C=C)][\mathrm{H}\cdot]} \approx \frac{5\cdot 10^3\cdot 15}{3\cdot 10^9[M(C=C)]} \approx \frac{2.5\cdot 10^{-5}}{[M(C=C)]}.$$

(Figure: Figure 2. Yield of gaseous products of hexane radiolysis as a function of irradiation dose. P—yield of gaseous products in ml of gas per ml of liquid n-hexane, D—irradiation dose in eV/ml.)

Fig. 2. Yield of gaseous products of hexane radiolysis as a function of irradiation dose. P—yield of gaseous products in ml of gas per ml of liquid n-hexane, D—irradiation dose in eV/ml.

Thus, the rates of these reactions become approximately equal when the concentration of unsaturated compounds in the solution reaches $2.5\cdot 10^{-5}$ mole/liter. Therefore, the pronounced nonlinearity of the yield of gaseous olefins (propylene, butene-1) is apparently explained by the hydrogenation reaction (Table 1). We note that under the experimental conditions ethylene is located, for the most part, in the gas phase.

On the basis of the experimental data presented in Table 1, the values of the radiation-chemical yield G (mole/100 eV) for the gaseous products of radiolysis were calculated and are summarized in Table 2.

Table 2

Product name	Mole/100 eV	Mole, %
Methane	0.41	11.0
Ethane	0.82	22.0
Ethylene	0.62	16.6
Propane	0.68	18.2
Propylene	0.31	8.3
Butane	0.65	17.5
Butene-1	0.24	6.4
	3.73	100.0

The G values obtained in the present work, with the exception of G for methane, are in general close to Futrell's data (^{10}) and differ from Dewhurst's data (^{3}). The reduced value of G for methane (^{10}) may be explained by the different sensitivity of the katharometer to methane and to the other hydrocarbons, allowance for which is not specifically stipulated in the procedure (^{10}). It should be noted that Krenz (^{11}) obtained $G = 0.4$ for methane.

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