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Abstract

Full Text

PHYSICAL CHEMISTRY

V. G. BEREZKIN, I. M. KUSTANOVICH, L. S. POLAK, and N. Ya. CHERNYAK

ON SOME FEATURES OF THE KINETICS OF RADIOLYSIS OF *n*-HEPTANE OVER A WIDE DOSE RANGE

(Presented by Academician A. V. Topchiev, November 18, 1959)

Numerous studies have been devoted to the radiolysis of normal hydrocarbons (¹⁻³). However, there is no systematic consideration in the literature of the yields of various radiolysis products over a wide dose interval. This question is elucidated in the present communication. In (¹) are described the radiation sources used, the method of filling and opening ampoules containing the irradiated hydrocarbon, the purification and degree of purity of the substance studied (heptane), and dosimetry. The present study was carried out at a temperature of 300° K in the dose interval $0.25-28 \cdot 10^{21}$ eV.

Figure 1 shows the yields of hydrogen, methane, and the C_2-C_5 fraction; the yields of H_2 and CH_4 were determined by the method described in (¹), while the method for determining the yields of C_2-C_5 is described below. In order to show more clearly the region of nonlinearity, the initial linear portions of the curves are continued by dashed lines. Deviation from linearity for H_2 and CH_4 begins near doses of $10-12 \cdot 10^{21}$ eV.

The composition of the C_2-C_5 fraction in the radiolysis products of heptane was studied by gas-liquid chromatography. In order to increase the sensitivity and resolving power of the chromatograph in the analysis of hydrocarbon radiolysis products, we, unlike a number of authors (³⁻⁵), used a sequential scheme employing two chromatographic units. On the first unit (stationary liquid phase—methylphenylpolysiloxane oil), the C_2-C_5 fraction was separated from higher radiolysis products and unreacted heptane. Detailed analysis of this fraction was carried out on the second unit by the method described in (⁵), at 0°. The sequential scheme makes it possible to carry out detailed chromatographic analysis of hydrocarbon radiolysis products after irradiation with relatively small doses. The sensitivity of the unit was $\sim 1 \cdot 10^{-3}$ ml of gas (carrier gas—helium). The reproducibility of the measurements was $\pm 5\%$. The calibration constant for quantitative analysis was determined with an accuracy of $\pm 10\%$.

Fig. 1. Dependence of the yield of hydrogen (1), methane (2), and hydrocarbons C_2-C_5 (3) on absorbed energy.

Table 1

Fig. 1. Dependence of the yield of hydrogen (1), methane (2), and hydrocarbons C_2-C_5 (3) on absorbed energy

Figure 1: Fig. 1. Dependence of the yield of hydrogen (1), methane (2), and hydrocarbons C_2-C_5 (3) on absorbed energy

Fig. 2

Figure 2: Fig. 2

Dose	Dose $0.5 \cdot 10^{21}$ eV/ml: content in $[C_nH_{2n+2}]$ - fraction C_2-C_5 , %	Dose $0.5 \cdot 10^{21}$ eV/ml: difference in $[C_nH_{2n+2}]$ - $[C_mH_{2m}]$, $n+$ $m = 7$, %	Dose $0.5 \cdot 10^{21}$ eV/ml: yield, 10^{-4} g-mole/l	Dose $1.18 \cdot 10^{21}$ eV/ml: content in $[C_nH_{2n+2}]$ - fraction C_2-C_5 , %	Dose $1.18 \cdot 10^{21}$ eV/ml: difference in $[C_nH_{2n+2}]$ - $[C_mH_{2m}]$, $n+$ $m = 7$, %	Dose $1.18 \cdot 10^{21}$ eV/ml: yield, 10^{-4} g-mole/l
Ethane	2.12	15.9	11.3	5.98	17.1	14.4
Pentene	0.61	4.6	11.3	0.94	2.7	14.4
Pentane	3.10	23.3	16.2	7.75	22.2	15.3
Ethylene	0.94	7.1	16.2	2.41	6.9	15.3
Propane	2.54	19.1	15.0	7.87	22.5	19.3
Butylene	0.55	4.1	15.0	1.12	3.2	19.3
Butane	2.70	20.3	14.7	7.49	21.4	17.4
Propylene	0.75	5.6	14.7	1.40	4.0	17.4
Total	13.31	100.0	Avg. 14.3	34.96	100.0	Avg. 16.8

Since all data available in the literature ^(2,3) on the composition of gaseous products of hydrocarbon radiolysis were obtained by taking a sample of the irradiated product for further analysis by one method or another, which is associated with the possibility of errors in determining the gas composition due to the sampling process itself, as was noted in ⁽⁶⁾, we carried out experiments with irradiation of heptane in special small ampoules; their contents were introduced entirely into the gas-liquid chromatography apparatus by breaking the ampoule in a special inlet device of the chromatograph. Therefore the data obtained, presented in Table 1, are free of all errors associated with sampling. These data refer to relatively small integral irradiation doses. In the remaining experiments the C_2-C_5 fraction was sampled by the method described in ⁽⁶⁾.

Fig. 2. **A**—dependence of the ratio of unsaturated gases to saturated gases in the C_2-C_5 fraction on absorbed energy. **B**—dependence of the ratio of unsaturated hydrocarbons to their complementary saturated hydrocarbons on absorbed energy: 1 — C_2H_4/C_5H_{12} ; 2a — C_3H_6/C_4H_{10} ; 2b — $\alpha-C_4H_8/C_3H_8$.

In Fig. 1, graphs B, the dependence of the yield of products of the C_2-C_5 fraction is shown. Deviation from linearity occurs at doses of the same order as for H_2 . From consideration of the data on the ratio of unsaturated and saturated hydrocarbons in the C_2-C_5 fraction (Fig. 2), it is seen that in the dose interval

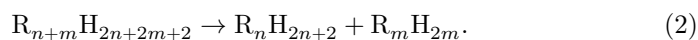
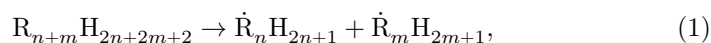
Fig. 3. Dependence of the yield of unsaturated (1) and saturated (2) hydrocarbons C₂–C₅ on absorbed energy

Figure 3: Fig. 3. Dependence of the yield of unsaturated (1) and saturated (2) hydrocarbons C₂–C₅ on absorbed energy

0.25–10 · 10²¹ eV the fraction of unsaturated compounds decreases from ~35 to ~8%; this occurs owing to the sharp nonlinearity of the yield of unsaturated gases, which sets in already at very small doses (Fig. 3).

It may be assumed that the formation of light hydrocarbons occurs through the decomposition of the molecule of the initial hydrocarbon into two radicals according to reaction (1), with subsequent formation from them of saturated hydrocarbons

upon recombination with an H atom or another radical, or by decomposition of the molecule into a saturated and an unsaturated fragment according to reaction (2):



The formation of unsaturated gases at room temperature is possible, evidently, only by reaction (2), since the assumption of another route for their formation—by the decomposition reaction of alkyl radicals or their disproportionation—is less probable because of the presence of an activation barrier in these reactions. Judging from the fact that at low doses, when secondary processes play a smaller role, the ratio of unsaturated gases to saturated ones is 0.35 (and at still lower doses, probably even higher), it may be considered that rupture of the C–C bond of the molecule of the initial hydrocarbon according to reaction (2) is in any case no less probable than according to reaction (1). If the radicals obtained by reaction (1) enter into recombination with other radicals with probabilities depending only on their concentrations, then the saturated hydrocarbons formed in this process that “complement” one another (C₂ and C₅, C₃ and C₄) must be obtained in equivalent amounts. Consequently, taking into account that reaction (2) also yields saturated hydrocarbons in equivalent amounts with the complementary unsaturated ones, we must obtain the following equalities:

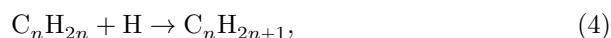
Fig. 3. Dependence of the yield of unsaturated (1) and saturated (2) hydrocarbons C₂–C₅ on absorbed energy

$$[C_2H_6] - [C_5H_{10}] = [C_5H_{12}] - [C_2H_4]; \quad [C_3H_8] - [C_4H_8] = [C_4H_{10}] - [C_3H_6]. \quad (3)$$

Fig. 4. Dependence of the yield of liquid unsaturated compounds on absorbed energy: 1—olefins (total) according to IR spectra (1a) and bromine numbers (1b); 2—trans-olefins; 3—dienes; 4— α -olefins; 5—vinylidene structures

Figure 4: Fig. 4. Dependence of the yield of liquid unsaturated compounds on absorbed energy: 1—olefins (total) according to IR spectra (1a) and bromine numbers (1b); 2—trans-olefins; 3—dienes; 4— α -olefins; 5—vinylidene structures

The corresponding differences are given in Table 1. Analysis of the data in Table 1 shows that equalities (3) do indeed hold, which is a substantial confirmation of the proposed scheme. The nonlinearity of the yield of unsaturated gases even at low doses can be explained by the fact that, since the concentration of unsaturated compounds very rapidly begins to become comparable with, and even to exceed, the stationary concentration of radicals, reaction with H (or other radicals) becomes possible.



since the unsaturated gases formed remain for the most part dissolved in the liquid phase. This reaction competes with the reaction of recombination of H atoms with one another and with radicals. The consumption of atomic hydrogen in reaction (4) should lead to a violation of the linearity of the yield of molecular hydrogen; but, since the absolute amounts of unsaturated compounds are considerably smaller than the amount of H, in practice we observe linearity of the hydrogen yield up to $1 \cdot 10^{22}$ eV, although, strictly speaking, nonlinearity

(i.e., the occurrence of secondary reactions) for all products should evidently begin almost from the very start of irradiation. The observed region of linearity of the yields is approximate, determined by the sensitivity of the analytical methods, and is significant only for estimating the dose interval in which a reasonable determination of the radiation-chemical yields of radiolysis products is possible; the observed nonlinearity of the curves in Fig. 1 is probably due to the protective action of unsaturated compounds.

The radiation yields, calculated from the linear portions of the curves for heptane radiolysis, are as follows (molecules/100 eV): H_2 4.5, CH_4 0.2, saturated hydrocarbons $\text{C}_2\text{—C}_5$ 1.6, unsaturated hydrocarbons $\text{C}_2\text{—C}_5$ (calculated from the slope of the tangent at the beginning of the curve) 0.4, liquid unsaturated compounds 2.0.

Fig. 4. Dependence of the yield of liquid unsaturated compounds on absorbed energy: **1**—olefins (total) according to IR spectra (**1a**) and bromine numbers (**1b**); **2**—trans-olefins; **3**—dienes; **4**— α -olefins; **5**—vinylidene structures.

Fig. 4 shows the dependence of the yield of various liquid olefins and dienes on dose. The various olefin structures were identified and their quantities determined from infrared absorption spectra on an IKS-14 spectrophotometer with

a NaCl prism. The spectra were recorded with a layer thickness of 0.1 mm. The greatest yield is given by trans-olefins ($\nu = 865 \text{ cm}^{-1}$, $E = 105$), considerably less by α -olefins ($\nu = 0.912 \text{ cm}^{-1}$, $E = 125$) and vinylidene structures ($\nu = 889 \text{ cm}^{-1}$; $E = 140$). The relative error in determining olefins of each structure does not exceed $\pm 8\%$. The olefin content calculated by summing the concentrations of the indicated structures agrees well with the data for olefin determination by the bromine method. The concentration of dienes was determined from absorption spectra with an ISP-28 quartz spectrograph by the photographic method in the region of 2300 \AA . The molar extinction coefficient was determined from heptadiene and was equal to 10^3 . Deviation from linearity for olefin formation occurs near doses of $10\text{--}12 \cdot 10^{21} \text{ eV}$ (Fig. 4), analogously to the curve for H_2 .

It is interesting to note that among the liquid unsaturated compounds (even at a dose of only $\sim 1 \cdot 10^{21} \text{ eV}$) 20% are heavy unsaturated compounds (with more than 10 carbon atoms) (7).

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