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Abstract

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ON THE RADIOLYSIS OF HEPTANE

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The article considers the γ-radiolysis of normal heptane in the liquid phase and the radiolysis of a solution of dibenzyl sulfide in heptane. The main aims of the investigation were: to establish the exact kinetics of radiolysis in the initial regions, in particular to determine the influence of an interruption in irradiation, and also to establish the detailed composition and yield of gas over a broad interval of doses (more than three orders of magnitude).

The addition of dibenzyl sulfide ($5.011 \cdot 10^{-4} M$)* to heptane was made in order to clarify the features of the behavior of aromatic sulfur compounds in a radiation field and to determine the influence of the presence of such additives on the radiolysis of paraffins.

The following radiation sources were used: a) at small doses—an RUP-3 X-ray apparatus operating under the following conditions: voltage 300 kV, tube current** 5 mA, focusing current—0.75 A. Under these conditions the dose rate in the irradiation cell, determined by a ferrous sulfate dosimeter, was about $3 \cdot 10^{15}$ eV/cm$^3 \cdot$ sec; b) at large doses the irradiation was carried out on installations with Co^{60}.

To study the kinetics of radiolysis at small doses, the following procedure was used. An annular irradiation cell made of Pyrex was placed directly at the anode of the tube. The upper part of the cell was connected through a short transition piece to a membrane manometer, the readings of which were recorded by means of a differential photocell on an EPP-09 self-recording potentiometer***. The sensitivity of the pressure measurement was $5 \cdot 10^{-2}$ mm Hg per 1 mm on the EPP-09 chart. Irradiation was carried out in two cells, the volumes of liquid in which were respectively 30 and 8 ml. The temperature during irradiation was maintained at $9 \pm 0.05^{\circ}$ by means of a Heppler ultrathermostat; constancy of temperature was controlled automatically. During irradiation with Co^{60}, the product was placed in special ampoules made of zirconium glass.

Commercial heptane was purified until practically complete transparency in the ultraviolet was attained. Possible impurities of higher and lower paraffins were not detected in mass-spectrometric analysis****. Dibenzyl sulfide was synthesized by the usual method, repeatedly recrystallized, and had constants and an ultraviolet-region spectrum coinciding with tabulated values. Before

irradiation all samples were freed from dissolved air by repeated freezing with evacuation by a diffusion pump. For carrying out gas analyses, a gas-liquid chromatography method was used, in its main features coinciding with that described in ([2]). This method permits analysis of 0.5 cm^3 of gas (up to C_5 inclusive) with relative accuracy for each compo-

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* All subsequent data refer to a solution of this concentration.
** A BPV-400 tube with an annular radiation exit was used.
*** Our circuit is a modification of the method of G. I. Kosourov ([1]).
**** The authors are grateful to G. D. Galpern and T. S. Novozhilova for carrying out the spectral measurements and to R. A. Khmel' nitskii for the mass-spectrometric analysis.

oil from 2 to 5% and with high sensitivity. It should be noted that the analysis and determination of the yields of radiolysis gases require careful methodological development, since even small methodological inaccuracies can lead to contradictory results in gas analysis ([3,4]).

Fig. 1. Kinetics of radiolysis at small doses. *a*—continuous irradiation; *b*—irradiation with an interruption.

At small doses, a direct proportionality of gas yield to irradiation time was observed. Cessation of irradiation synchronously caused cessation of gas evolution as well. When irradiation was resumed, the gas-evolution line was in fact a continuation of the initial straight line (Fig. 1). Thus, radiation "hysteresis" in gas evolution is not detected with very high accuracy. Direct measurement of the amount of gas by our method showed that the amount of hydrogen and methane dissolved in heptane is small and that Henry' s law is obeyed. Figure 2 shows the dependence of the yields of hydrogen and methane on dose for pure heptane and for a solution of dibenzyl sulfide. In order to combine data corresponding to a wide range of integral doses, while at the same time preserving the form of the curve in ordinary coordinates at small degrees of radiolysis, the abscissa and ordinate axes plot, respectively,

$$\ln(1+a) \quad \text{and} \quad \ln\left(1+\frac{D_D}{10^{21}}\right),$$

where a is the yield of methane and hydrogen in cm^3 per 10 ml of substance, and D_D is the dose according to the ferrous-sulfate dosimeter. Deviations from the linearity corresponding to the curves in Fig. 2 begin at integral doses of the order of $D_D = 10^{21}$ eV/ml. Figure 2 also shows that dibenzyl sulfide plays a protective role with respect to radiolysis of heptane: the yield of the hydrogen-methane fraction decreases by approximately 10% in the linear region.

For determining the absolute values of the radiation-chemical yields (G), the doses obtained with the ferrous-sulfate dosimeter were recalculated to the dose

in n-heptane, taking into account that absorption is directly proportional to the density and effective atomic number of heptane, referred to the density and effective atomic number of the dosimetric system. Thus, the dose in heptane is

$$D_{C_7H_{16}} = D_D \frac{\rho_{C_7H_{16}} \bar{Z}_{C_7H_{16}}}{\rho_D \bar{Z}_D}, \quad \text{where } \bar{Z} = \sqrt[2.94]{\frac{\sum nZ^{3.94}}{\sum nZ}}$$

Fig. 2. Kinetics of the evolution of hydrogen and methane during radiolysis. The discontinuous portions of the curves near the origin correspond to experimental data at small doses. The curves correspond to the linear law of gas evolution. I and squares—pure heptane; II and crosses—solution of dibenzyl sulfide in heptane. a—in $cm^3/10$ ml, D_D—in eV $\cdot 10^{-21}$.

and ρ_i are densities ([5]). Since our measurements have shown that nonlinear effects already occur at a dose of 10^{21} eV/ml, while at smaller doses we were able to measure accurately only the yields of hydrogen and methane, values of G are given only for these gases: $G(H_2) = 4.9$; $G(CH_4) = 0.22$. The value $G(H_2) = 4.9$ is fairly close to the value reported in ([4]) ($G(H_2) = 4.7$). It should be noted that the yield of methane reported in ([4])

$G(CH_4) = 0.09$, and also the preservation of the linear dependence of the yield on dose, do not correspond to our data,* as is evident for pure heptane from Table 1.

Let us turn to consideration of the gas fraction C_2–C_5, which for pure heptane at an integral dose $D_D = 3.25 \cdot 10^{22}$ eV/ml reaches 20.5 mole % of the total gas yield. Table 2 gives the results of gas analysis (mole percent).

Table 1

D_D (eV/ml)	Yield of fraction 1B ($cm^3/10$ ml)	Composition of fraction 1: H_2 (mole %)	Composition of fraction 1: CH_4 (mole %)
$1.6 \cdot 10^{19}$	0.15	Analysis was not performed	Analysis was not performed
$3.2 \cdot 10^{19}$	0.30	95.9	4.1
$4 \cdot 10^{21}$	34	96.6	3.4
$3.25 \cdot 10^{22}$	193	98	2

We shall make the following observations in connection with the data presented above.

1. Nonlinear effects begin at integral doses $D_D = 10^{21}$ eV/ml and occur for all components. The nonlinearity for methane, in particular, can easily be explained if interaction of the radical CH_3 with radiolysis products is assumed, which is consistent with general ideas about the course of the process.

2. An exceptionally large role in the radiolysis of alkanes is played by the process of direct rupture of C–C bonds, both with the formation of alkyl radicals and with the direct formation of final products–saturated and unsaturated.

Table 2

Composition of the radiolysis gases

Components	*n*-heptane, D_D (eV/ml): $3.2 \cdot 10^{19}$*	*n*-heptane, D_D (eV/ml): $4 \cdot 10^{21}$*	*n*-heptane, D_D (eV/ml): $3.25 \cdot 10^{22}$	Solution of dibenzyl sulfide in heptane, D_D (eV/ml): $2.4 \cdot 10^{21}$	Solution of dibenzyl sulfide in heptane, D_D (eV/ml): $4 \cdot 10^{21}$
Hydrogen	95.9	96.6	79.5	70.1	73.27
Methane	4.1	3.4	1.6	2.37	1.54
Ethane		97.2	3.2	6.46	8.03
Ethylene		97.2	0.22	2.30	8.03
Acetylene		2.8	0.02	4.37	0.09
Propane			4.57	3.30	5.27
Propylene			0.32	1.41	0.85
n-Butane			4.49	3.98	3.31
i-Butane			0.09	–	–
i-Butene			0.18	1.53	1.36
n-Butene-1			0.18	1.53	1.36
n-Butene-2			0.26	–	–
i-Pentane			0.22	–	–
3-Methylbutene-1			0.22	–	–
n-Pentane			4.83	4.18	6.29
2-Methylbutene-1			0.3	–	–

Components	n-heptane, D_D (eV/ml): $3.2 \cdot 10^{19}$*	n-heptane, D_D (eV/ml): $4 \cdot 10^{21}$*	n-heptane, D_D (eV/ml): $3.25 \cdot 10^{22}$	Solution of dibenzyl sulfide in heptane, D_D (eV/ml): $2.4 \cdot 10^{21}$	Solution of dibenzyl sulfide in heptane, D_D (eV/ml): $4 \cdot 10^{21}$
2-Methylbutene-2			0.2	–	–
Hydrogen sulfide			–	–	–
Total gas yield (cm^3/10 ml)			234.5	24.9	36.6

* In this column the composition is given for individual fractions. No other analyses were carried out in these experiments.

This part of radiolysis resembles the thermal cracking of hydrocarbons under conditions of a short-duration but powerful thermal shock.

* Deviations from the linear law occur for both hydrogen and methane, and for methane to a greater extent. The indicated discrepancy in the results is explained by the inaccuracy of determining small amounts of methane by the mass-spectrometric method used in (4). In fact, all of Dewhurst' s analyses belong to the nonlinear region.

3. The presence of acetylene in the radiolysis gases should be noted (in the radiolysis of alkanes, acetylene has been detected for the first time); its relative amount decreases with increasing integral dose. The concentration of other lower olefins also decreases in the course of radiolysis, which indicates the major role of secondary reactions of the lower olefins. In general, the composition of the gas indicates enrichment of the liquid phase with hydrogen during radiolysis.

4. An important fact is the wide range of radiolysis gases, among which there are relatively many isomeric structures (probably of secondary origin). To our knowledge, the complete composition of the radiolysis gases is presented for the first time.

5. Hydrogen sulfide is absent from the radiolysis gases of a solution of dibenzyl sulfide in heptane. This indicates that the decomposition of dibenzyl sulfide with evolution of hydrogen sulfide did not exceed, in the cases con-

sidered, 10% of the total amount of dibenzyl sulfide. Thus, the protection in this case may be based on excitation transfer.

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