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## Abstract

## Full Text

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# ON RADIATION-THERMAL TRANSFORMATIONS OF NORMAL ALKANES IN THE LIQUID PHASE

In this work we investigated radiation-thermal transformations of *n*-alkanes in the liquid phase, using *n*-paraffin $C_{34}H_{70}$ as an example. As was shown earlier ([1,2]), the dependence of radiation-thermal decomposition in the liquid phase on temperature has a specific form with two "Arrhenius" intervals, the first of which (up to temperatures of 300°) corresponds to a small activation energy (less than 3 kcal/mole), and the second (from 300° to the onset of thermal decomposition) to an activation energy of the order of 25 kcal/mole. Study of the radiolysis of an individual hydrocarbon in these temperature intervals made it possible to estimate concretely a number of characteristics of elementary acts occurring in radiation-thermal transformations of alkanes after thermalization of radicals, and also to estimate the concentrations of the latter.

Fig. 1. Dependence of the yields of gaseous products of radiolysis of *n*-tetratriacontane on temperature:
1 –$H_2$; 2 –$CH_4$; 3 –$C_2$ hydrocarbons;
4 –$C_3H_8$; 5 –$C_3H_6$; 6 –$C_4H_{10}$; 7 –$C_4H_8$ (mean values)

The experiments were carried out in the channel of a water-water type nuclear reactor in heated quartz ampoules by the method described earlier in ([1]), at an integral dose of $6 \cdot 10^{21}$ eV/g and temperatures of 150°, 250°, 280°, 315°, 380°. Up to the indicated value of the integral dose, a linear dependence of the radiation-chemical yields ($G_i$) of the greater part of the radiolysis products on dose is observed within the limits of analytical accuracy ([3])*.

## Table 1

Radiation-chemical yields
(molecules/100 eV) of gaseous radiolysis products
(mean of 8 experiments)

| $G$, molecules/100 eV | 150 | 250 | 280 | 315 | 380 |
|---|---|---|---|---|---|
| $G_{H_2}$ | 4.2 | 4.3 | 4.4 | 4.3 | 4.1 |
| $G_{CH_4}$ | 0.027 | 0.041 | 0.059 | 0.14 | 1.06 |
| $G_{\Sigma C_2}$ | 0.10 | 0.15 | 0.19 | 0.38 | 2.36 |
| $G_{C_3H_8}$ | 0.054 | 0.082 | 0.12 | 0.33 | 2.1 |
| $G_{C_3H_6}$ | 0.013 | 0.016 | 0.032 | 0.13 | 0.81 |
| $G_{C_4H_{10}}$ | 0.050 | 0.075 | 0.11 | 0.29 | 1.6 |
| $G_{C_4H_8}$ | 0.012 | 0.012 | 0.023 | 0.076 | 0.50 |
| $G'_{pol}$ | 4.0 | 4.0 | 3.9 | 3.9 | 3.9 |

Data on the analysis of the gaseous products of the experiments, as well as data on the number of molecules of the initial hydrocarbon converted into polymers ($G'_{pol}$), are given in Table 1. The accuracy of determining the $G_i$ values for the different products was $\pm 5\%$. The hydrogen yield is approximately equal to $G'_{pol}$; both quantities change little with increasing temperature. In this connection, in the subsequent treatment of the experimental results, in order to eliminate errors in dosimetry, the data on the formation of various gaseous products were taken in the form of ratios—

* Analysis of gaseous and liquid products was carried out by means of gas-liquid chromatography ([4,5]). The quantity of high-boiling products ( “polymers” ) was determined by molecular distillation in vacuum at $10^{-4}$-$10^{-5}$ mm Hg. With the aid of···

of the value of the yield of some product to the corresponding yield $G'_{pol}$. The dependence of such reduced yields on temperature is shown in Fig. 1. The activation energies of the reactions of formation of various radiolysis products are given for different regimes of radiation-thermal transformations in Table 2.

In the liquid products of radiolysis, hydrocarbons up to $C_{10}$ inclusive were found. The main portion consists of saturated hydrocarbons of normal structure. Hydrocarbons of cyclic structure were also identified: cyclopentane, cyclopentadiene. Among the $C_6$—$C_7$ hydrocarbons there are cyclohexene, cyclohexadiene, and the corresponding $C_7$ hydrocarbons. The dependence of the increase in the concentration of dienes on temperature is given in Fig. 2. IR spectra of samples irradiated at temperatures of 150°, 250°, 280°, 315°, and 380° show that during radiolysis trans-olefin groups are formed, the concentration of which practically does not change with increasing temperature and amounts to 4-8%. At temperatures above 300°, vinyl groups of the type $-HC = CH_2$ appear, the

concentration of which is 1-2%. With increasing temperature, in the solid products of radiolysis there is an increase in the number of methyl groups (see Fig. 2): at 150° on average two methyl groups are formed per molecule of the initial tetratriacontane, while at 380° the number of methyl groups increases to 3-4. The effective activation energy of the corresponding process is 10 kcal/mole. In the IR spectra of the polymers, the presence of bonds between two tertiary carbon atoms was also detected, their amount being 1-2%. With increasing temperature, at the same integral dose, a decrease in the molecular weight of the polymers occurs. At 150—200° the molecular weight of the polymers is approximately equal to twice the weight of the initial hydrocarbon, while with an increase in temperature to 380° the molecular weight of the polymers decreases by 25%.

**Table 2**

**Activation energy for the formation of gaseous products in the I and II intervals of radiation-thermal transformations and pre-exponential factors of the rate constants for decomposition of iso-radicals**

| $E$ activation | $CH_4$ | $C_2$ | $C_3H_8$ | $C_3H_6$ | $C_4H_{10}$ | $C_4H_8$ |
|---|---|---|---|---|---|---|
| I | 2.8 | 1.3 | 1.8 | 1.40 | 1.77 | 3.00 |
| II | 24.3 | 21.3 | 20.7 | 21.6 | 20.1 | 22.6 |
| $k_d^{0i}$ | $6 \cdot 10^{10}$ | $8 \cdot 10^9$ | $9 \cdot 10^9$ | $1 \cdot 10^{10}$ | $3 \cdot 10^9$ | |

Let us proceed to a discussion of the experimental results. The total transformation of tetratriacontane is made up of direct "molecular" destruction and reactions of thermalized radicals. Both direct destruction and the formation of primary radicals* are the result of radiation-chemical processes proceeding with energies much greater than thermal energies and involving reactions of ions and ion-radicals. The rates of these processes may be regarded as independent of temperature. At the same time, the rates of further reactions of the thermal radicals formed depend substantially on temperature. The main results of the action of radiation on tetratriacontane will be, after dissipation of the excess energy and neutralization of ions, ruptures of C–C bonds and abstraction of hydrogen atoms. In the latter case iso-radicals ($R_i$) should be formed predominantly, in which the free valence is located at a secondary carbon atom, and the hydrogen atom that has been abstracted will usually–

by means of IR and UV spectroscopy of the solid products of radiolysis, the amounts of olefins, dienes, and hydrocarbons of isomeric structure formed were determined. After special purification of the initial tetratriacontane, the spectra showed a complete absence of impurities. The authors thank M. M. Kusakov, N. A. Shimanko, and M. V. Shishkina for carrying out the spectral analyses.

* The primary thermalized products of the action of radiation are called in this work products obtained after dissipation of excess suprathermal energy,

Figure 2. Dependence of the yields of certain solid products of radiolysis of $n$-tetratriacontane on temperature: 1 —alicyclic dienes; 2 —cyclic dienes; 3 — increase in the number of methyl groups in the solid products of radiolysis. (These three curves express the dependence of relative yields on temperature.) 4 —polymers

Figure 2: Figure 2. Dependence of the yields of certain solid products of radiolysis of $n$-tetratriacontane on temperature: 1 —alicyclic dienes; 2 —cyclic dienes; 3 —increase in the number of methyl groups in the solid products of radiolysis. (These three curves express the dependence of relative yields on temperature.) 4 —polymers

but before the occurrence of secondary reactions possible at the experimental temperature.

carry away the excess energy and rapidly enter, in the liquid phase, into substitution reactions with the formation of isoradicals. Thus, the primary thermal radicals formed both by this path and upon rupture of C–C bonds will exist mainly in the form of pairs of radicals constituting a liquid cage.* We shall characterize the temperature-independent rate of formation of primary thermal radicals in the cage by the radiation-chemical yields $G_{(R_i)}$ and $G_{R(n)}$, where

$$G_{(R_i)} + G_{(R_n)} = G_{(R)}.$$

The principal route by which radicals disappear in the cage is their recombination (or disproportionation), as well as the escape of radicals from the cage owing to diffusion. The role of chain transfer is comparatively insignificant. As was indicated, the content of unsaturated hydrocarbons with a number of carbon atoms equal to, or close to, the number of carbons in the initial hydrocarbon is almost independent of temperature and amounts to 10-20% by weight of the amount of polymers formed. This corresponds to the fact that the rate of disproportionation is 20-40% of the recombination rate for radicals of the type under consideration ([6]). Writing the balance equation for the quasi-stationary concentrations of iso- and normal radicals in the liquid cage $[(R_i)]$ and $[(R_n)]$ and outside the cage (see [2]), and retaining only the principal routes of radical transformation, we arrive at the following equations for the yield of the lower unsaturated and saturated hydrocarbons:

**Fig. 2.** Dependence of the yields of certain solid products of radiolysis of $n$-tetratriacontane on temperature: **1** —alicyclic dienes; **2** —cyclic dienes; **3** —increase in the number of methyl groups in the solid products of radiolysis. (These three curves express the dependence of relative yields on temperature.) **4** —polymers

$$G^m_{C_mH_{2m}} - G^{0m}_{C_mH_{2m}} \approx \delta^m G_{(R_n)} \tau/(2\tau'_D) + (\delta^m + \beta'^m/2) k^i_d [\bar{R}]/I, \qquad (1,1)$$

$$G^m_{C_mH_{2m+2}} - G^{0m}_{C_mH_{2m+2}} \approx \gamma^m G_{(R_n)}\tau/(2\tau_D) + k^i_d\gamma^m[\bar{R}]/I. \qquad (1,2)$$

Here the quantities $G^0_i$ are the yields of the corresponding direct processes, independent of temperature; $\delta^m = k^m_d/k^n_d$ is the fraction of ruptures of the $m$-th C–C bond in the radicals $\bar{R}_n$ outside the cage; $\tau$ is the characteristic time of disappearance of a pair of radicals in the cage**; $\tau_D$ is the time characterizing the disappearance of a pair of radicals in the cage owing to diffusion; $k^i_d$ is the rate constant of the decomposition reaction of isoradicals; $[\bar{R}]$ is the concentration of hydrocarbon radicals outside the cage; $I$ is the dose rate (eV per unit volume per second); $\gamma^m$ is the fraction of normal radicals with $m$ carbon atoms; $\beta'^m$ is a factor characterizing the probability of formation of isoradicals in substitution reactions outside cages with such a position of the free valence that, upon decomposition of $R_i$, a short radical $\bar{R}_n$ is formed ($\Sigma\beta'^m = \beta$). It follows from the equations given above that the strong temperature dependence in the second interval of radiation-thermal transformations for both lower unsaturated and lower saturated products is due to

* In this case the formation of biradicals is also possible; these subsequently isomerize into olefins or form cyclic structures. The occurrence of the cyclization reaction was noted by us earlier in work ([3]).

** The characteristic time for disappearance of a pair of radicals in the cage occurs both by recombination and by diffusion: $1/\tau = 1/\tau_f + 1/\tau_D$, where $\tau_f$ is the time characterizing the disappearance of a pair of radicals in the cage owing to recombination.

by the decomposition of isoradicals outside the cage, i.e., proportional to $k^i_d$. Therefore, both processes have close activation energies. From equations (1) one can estimate the pre-exponential factor for the decomposition reactions of alkyl radicals in a liquid (see Table 2). Thus, in the second interval of radiation-thermal transformations, where the term containing $k^i_d$ plays the main role, for $T > T^*_c$

$$k^{i0}_d \simeq G_i\sqrt{I}\exp(E/RT)\sqrt{k_t(1/\alpha_i)}(1/\sqrt{G_{\overline{R}}}), \qquad (2)$$

where $G_{\overline{R}}$ is the yield of hydrocarbon radicals in the liquid outside the cage; $E$ is the activation energy for formation of the $i$-th gaseous product in the second interval of radiation-thermal transformations; the quantity $\alpha_i$ is estimated from the composition of the destruction products; the value of $k_t$ was taken to be $10^{-12}$ cm$^3$/molecule $\cdot$ sec. The yield of polymers, weakly dependent on temperature, is expressed by the equation: $G_{\text{pol}} = [G_{(R_i)} + G_{\overline{R}}]\Delta/2$, where $\Delta$ is the fraction of recombination reactions among the recombination and disproportionation reactions. If one takes $G_{\overline{R}} \simeq 3$, and $\Delta \simeq 0.8$, and substitutes the experimental value $G_{\text{pol}} = 2.5$, then the yield $G_{(R_i)}$ will be about 3 radicals per 100 eV. From the equations for the total balance of radicals in the cage and

outside the cage we obtain an equation relating the yields of radicals outside and inside the cage,

$$G_{(R)}/G_{\overline{R}} = 1 + \tau_D/\tau_t.$$

From this equation, assuming $G_{(R_i)} \simeq G_{\overline{R}}$, we obtain that $G_{(R_n)}/G_{\overline{R}} \simeq \tau_D/\tau_t$. From equations (1), (2), at $T \simeq T_c$, when the contribution of the terms weakly dependent on and independent of temperature becomes comparable with the contribution of the terms strongly dependent on temperature, we obtain, assuming $G^{om}_{C_mH_{2m+2}} < \gamma^m G_{(R_n)}\tau/2\tau_D$, that

$$\tau_D/\tau G_{(R_n)} = \tau_D/\tau_t G(\overline{R}^n) + 1/G_{(R_n)} \simeq \sqrt{I}\sqrt{k_t}/2k_d^i\sqrt{G_{\overline{R}}}|_{T\simeq T_c}.$$

Substituting the values of $I$, $k_d^i$ from the experimental data and the adopted values of $G_{\overline{R}}$ and $k_t$, we obtain that $1/G_{\overline{R}} + 1/G_{(R_n)} \simeq 0.4$. For $G_{\overline{R}} \simeq 3$ it follows that $G_{(R_n)} \simeq 14$, and the total yield of radicals in the cage is $G_{(R)} \simeq 17$ radicals per 100 eV. Under the conditions considered, the ratio $\tau_D/\tau_t \simeq 5$, i.e., the rate of radical recombination in the cage is comparable with the rate of radical diffusion. From the obtained estimates of radical yields in the liquid cage it follows that, in the cage, under the action of radiation, pairs of normal radicals are formed mainly (upon decomposition of the initial molecule at the C–C bond), but these radicals, upon recombination, again give the initial hydrocarbon molecule. Taking the size of the cage in the liquid to be equal to the size of a tetratetracontane molecule ($\sim 40$ Å), one can estimate the value of $\tau_D$, which turns out to be approximately $\tau_D \simeq d^2/\pi^2 D \simeq 5 \cdot 10^{-8}$ sec (here $D$ is the coefficient of self-diffusion of the hydrocarbon, approximately $10^{-6}$ cm$^2$/sec). With this value of $\tau_D$, the value of $\tau_t$ is $\sim 10^{-8}$ sec, and the stationary concentration of radicals in the cage will be $\sim 2 \cdot 10^9$ pairs of radicals/cm$^3$, or $4 \cdot 10^9$ radicals/cm$^3$. Outside the cage the stationary concentration of radicals is about $2 \cdot 10^{14}$ radicals/cm$^3$.

In addition to tetratetracontane, solutions of $n$-terphenyl in tetratetracontane were studied (from $10^{-1}$ to $10^{-6}$ $M$ $n$-terphenyl). The inhibiting action of $n$-terphenyl was observed only in the formation of diene compounds.

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* $T_c$ is the temperature of transition from the first interval of radiation-thermal transformations to the second.

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