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Yu. A. Kolbanovskii and B. A. Smirnov

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Abstract

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CALCULATION OF THE YIELDS OF PRODUCTS OF RADIOLYSIS OF ALKANES

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The aim of the present work was to formulate balance equations for products of alkane radiolysis in order to determine the content of various fractions from a limited number of experimental data. Of particular importance here is the calculation of the yield of the heavy residue, which is the most difficult to determine experimentally. In conclusion, a calculation is given of the balance of products of radiolysis of *n*-heptane in the linear and nonlinear regions, illustrating the application of the derived relations.

The principal products of radiolysis of alkanes are hydrogen, monoolefins, and also alkanes of normal and isomeric structure of various molecular weights with a number of carbon atoms C_x, where $x \gtreqless n$ (n is the number of carbon atoms in the initial hydrocarbon). Then the number of molecules after irradiation N_k is related to the initial number of molecules of the starting alkane N_0 by the relation

$$N_\mathrm{k} = N_0 + N'', \tag{1}$$

where N'' is the number of monoolefin molecules formed during radiolysis. In addition, another relation can be written for N_k:

$$N_\mathrm{k} = N_n + N_\mathrm{l} + N''_\mathrm{l} + N_\mathrm{t} + N''_x, \tag{2}$$

where N_n is the number of molecules of the initial alkane after radiolysis; N_l is the number of molecules of hydrogen and alkanes with $x < n$; N''_l is the number of molecules of monoolefins with $x < n$; N''_x is the number of molecules of monoolefins with $x \gtreqless n$; N_t is the number of molecules of alkanes with $C_{x>n}$.

From (1) and (2) it follows that

$$N_n = N_0 - (N_\mathrm{l} + N_\mathrm{t}) \tag{3}$$

or

$$N_{\mathrm{t}} + N_n = N_0 - N_{\mathrm{l}}. \tag{3'}$$

For practical purposes, the following relations may prove useful:

$$N_x = N_n + N_{\mathrm{t}} + N_x'' \tag{4}$$

or, taking into account (1) and (2),

$$N_x = N_0 + N_x'' - N_{\mathrm{l}}, \tag{5}$$

where N_x is the number of all molecules with $C_{x \geq n}$. Equations 1-5 are exact balance equations.

The subsequent discussion is carried out separately for the linear and nonlinear regions of radiolysis. By the linear region we shall understand the initial portion of radiolysis, in which secondary reactions of the final products are absent. Then, for the linear region, at a reaction-chain length of

with a conversion fraction close to unity, two limiting relationships can be written for calculating N_τ:

$$N_{\tau_1} = N_\ell - N''. \tag{6'}$$

$$N_{\tau_2} = N_\ell - N_x''. \tag{6''}$$

Equation (6′) is exact if the loss of free radicals occurs only by recombination. If, at the same time, a disproportionation reaction takes place, then equation (6′) gives underestimated results. Thus, in the general case, equation (6′) determines the lower limit of the yield of the saturated part of the heavy residue and, accordingly, the upper limit of the molecular weight of alkanes with $\mathrm{C}_{x>n}$.

Equation (6″) is exact if the loss of free radicals by recombination is equal to or greater than their loss by the disproportionation reaction. If the majority of free radicals perish in the disproportionation reaction, then (6″) gives overestimated results. Thus, in the general case equation (6″) determines the upper limit of N_τ and, accordingly, the lower limit of the molecular weight of alkanes with $\mathrm{C}_{x>n}$. Let us additionally note that in the linear region the inequality must be strictly satisfied:

$$N_{\mathrm{H2}} < N_x'' + N_\tau. \tag{7}$$

In the nonlinear region, when polymerization of unsaturated compounds with $\mathrm{C}_{x \geq n}$ has proceeded far, inequality (7) may fail to be satisfied.

To estimate the balance of radiolysis products of n-heptane in the linear region, we shall adopt the following values of radiation-chemical yields (in molecules per 100 eV of absorbed energy): $G(\mathrm{H_2}) = 4.9$; G (saturated decomposition products) $\simeq G$ (unsaturated decomposition products) $= 0.7$; G (monoolefins with $\mathrm{C}_{x \geq n}$) $= 2.0$. Then, according to $(6')$ and $(6'')$, we have, respectively, the lower and upper limits of the yield of the saturated part of the heavy residue: $G_1(\tau) = 2.9$ and $G_2(\tau) = 3.6$. However, the value $G_1(\tau)$ does not satisfy inequality (7), and we shall use the value $G_2(\tau)$.

Then, for 1 ml of the initial n-heptane at a dose of 10^{19} eV/ml, for example, we shall have: $N_0 = 683.8 \cdot 10^{-5}$ mol; $N_x'' = 0.033 \cdot 10^{-5}$ mol; $N_\ell = 0.093 \cdot 10^{-5}$ mol; $N_\ell'' = 0.012 \cdot 10^{-5}$ mol; $N_\tau = 0.06$ mol. According to (3), $N_n = 683.65 \cdot 10^{-5}$ mol and the degree of conversion of the initial n-heptane is

$$y = 100\,(N_0 - N_n)/N_0 = 0.022 \text{ mol. } \%.$$

Table 1 presents the yields of radiolysis products per 100 molecules of converted n-heptane.

Table 1

Yield of the principal radiolysis products of n-heptane, calculated per 100 molecules of converted initial substance

Converted n-heptane	Hydrogen	Hydrocarbons with number of molecules $\mathrm{C}_{x<n}$	Monoolefins C_7	Saturated hydrocarbons with number $\mathrm{C}_{x>n}$	Sum
In the linear region	In the linear region	In the linear region	In the linear region	In the linear region	In the linear region
100	53	15	22	39	129
In the nonlinear region	In the nonlinear region	In the nonlinear region	In the nonlinear region	In the nonlinear region	In the nonlinear region
100	55	18	44	28	145

We shall now use the derived relationships to calculate the balance of radiolysis products of n-heptane in the nonlinear region. The initial data for the calculation [1,2] are collected in Table 2.

From equation $(6'')$ we find the number of moles $N_\tau = 39.62 \cdot 10^{-5}$, and from equation (3) $N_n = 542.66 \cdot 10^{-5}$ moles/MJ (with the number of g-atoms of carbon $N_\mathrm{C} = 3798.62 \cdot 10^{-5}$ and the number of g-atoms of hydrogen $N_\mathrm{H} = 8682.52 \cdot 10^{-5}$). Let us now calculate the elemental composition and the average molecular weight of the alkanes with the number $C_{x \geq n}$. The calculation gives the averaged formula $C_{11.35}H_{24.7}$ and the average molecular weight $\overline{M} = 161$, which, as emphasized earlier, is the lower limit of the values $\bar{x}$ and $\overline{M}$. The degree of conversion of the initial heptane in this case is 20.8 mole %.

Table 2

Components	$1 \cdot 10^5$mol/MJ	$1 \cdot 10^5$ g-at.C	$1 \cdot 10^5$ g-at.H
H_2	77.77	–	155.54
N_1	101.52	94.79	392.6
N_1''	2.02	8.81	17.52
N_x''	61.9	433.3	866.6
N_0	683.8	4786.6	10940.8

Table 1 gives the yields of the main radiolysis products in molecules per 100 molecules of converted n-heptane in the nonlinear region at a dose of 650 Mrad (without recalculation to n-heptane).

Comparison and analysis of the data obtained show that, with increasing dose, the yield of hydrogen continues to follow a law close to linear. For the other components the nonlinearity is very substantial: the yield of the limiting fraction of the heavy residue decreases, whereas the yield of unsaturated hydrocarbons with $C_{x \geq n}$ increases sharply. This indicates a considerable degree of unsaturation of the heavy residue in the nonlinear region. With increasing dose, the total number of molecules formed upon decomposition of 100 molecules of the starting substance increases. This indicates that, in the course of radiolysis, the average molecular weight of the product will decrease.

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Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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CITED LITERATURE

1. A. M. Brodskii, Yu. A. Kolbanovskii et al., DAN, **122**, 1035 (1958).
2. B. A. Smirnov, *Optics and Spectroscopy*, No. 4 (1960).

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

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