ISOTOPE EFFECT IN THE RADIOLYTIC FORMATION OF HYDROGEN FROM POLYETHYLENE

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Abstract

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ISOTOPE EFFECT IN THE RADIOLYTIC FORMATION OF HYDROGEN FROM POLYETHYLENE

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It is known that the principal gaseous product of the radiolysis of saturated hydrocarbons in the condensed phase is hydrogen. Thus, for example, the fraction of hydrogen in the gaseous products of polyethylene radiolysis at doses of 10-200 Mrad is 85-98% (^{1}). Numerous investigations have been carried out on the radiation-chemical transformations of alkanes, devoted to the study of the mechanism of hydrogen formation. On the basis of a comparison of the radiation yield of radicals (measured by the method of radical acceptation by J_2 additives) and the radiation yield of hydrogen, it was concluded that hydrogen in the radiolysis of alkanes is formed by two routes: radical and molecular, with approximately one half of the hydrogen being formed by each route (see, for example, (^{2})). This conclusion is confirmed in studies of the radiolysis of polyethylene, in which the radiation yields were measured for radicals formed upon detachment of a hydrogen atom (^{3}), and for double bonds (^{1}), formed upon elimination of molecular hydrogen. The fraction of hydrogen formed by the molecular route in the radiolysis of ethane in the gas phase was first determined by Dorfman (^{4}), who studied the radiolysis of mixtures of C_2H_6 and C_2D_6. The isotope method was also applied in the work of Nevitt and Remsberg (^{5}), and of Dyne and Jenkinson (^{6}), who investigated the radiolysis of cyclohexane in the liquid phase.

In the works (^{4,5}) it was assumed that the radiation yields of H_2 formed by the molecular route from light hydrocarbon molecules and of D_2 from deuterated molecules differ insignificantly from one another.

In the present work, measurements were made of the radiation yields of H_2 and D_2 formed by the molecular route, respectively, from polyethylene and deuteropolyethylene.

High-pressure polyethylene and deuteropolyethylene with a softening temperature of 126-127° and a D isotope content equal to 98 at.% were chosen as the objects of study. Mixtures $(C_2H_4)_n$ and $(C_2D_4)_n$ were prepared by dissolving known quantities of these substances in toluene (chemically pure grade) at a temperature close to the boiling point of toluene, followed by precipitation of the polyethylene with methyl alcohol. The precipitate was filtered off and thoroughly washed with methyl alcohol. After this, the mixture was dried to constant weight. Samples of the mixture, having the form of a white loose powder and weighing 0.05–0.1 g, were fused into copper cups 8 mm in diameter, which were then placed in a metal demountable ampoule, where irradiation was carried out with electrons of energy 1.6 MeV. The absorbed dose was calculated from the electron current and the stopping power of polyethylene, equal to 1.92 $\mathrm{MeV/g\cdot cm^2}$ for $(C_2H_4)_n$ and 1.68 $\mathrm{MeV/g\cdot cm^2}$ for $(C_2D_4)_n$. It was assumed that the energy absorbed by the molecules $(C_2H_4)_n$ and $(C_2D_4)_n$ in the mixture is proportional to their electron fractions. The amount of gas evolved during radiolysis was measured by means of a U-shaped manometer, the working liquid in which was D-4 grade oil. The manometer was

graduated according to the readings of a mercury manometer. At various times during radiolysis, gas samples were taken and then analyzed on an MX-1302 mass spectrometer. In the calculations, the mass spectra of D_2 and HD reported in (^{7}) were used. The HD content in the samples was in all cases sufficiently large to neglect the formation of H_3^+ ions in the mass spectrometer. Special experiments showed that, for our purposes, there was no appreciable isotopic exchange in the mass spectrometer.

The principle of the method used in the work is analogous to that used by Dainton and Jenkinson. In the radiolysis of mixtures of $(C_2H_4)_n$ and $(C_2D_4)_n$, the amounts of H_2 and D_2 formed by the molecular route depend linearly on the concentrations of $(C_2H_4)_n$ and $(C_2D_4)_n$ (henceforth we shall denote these concentrations by C_H and C_D). The dependence of the amounts of H_2 and D_2 formed by the radical route on C_H and C_D will be quadratic. The general scheme of the processes by which hydrogen can be formed is as follows:

$$\begin{aligned}
(C_2H_4)_n &\rightsquigarrow H_2 + M_1 && G_1(H)\\
(C_2D_4)_n &\rightsquigarrow D_2 + M_2 && G_1(D)\\
(C_2H_4)_n &\rightsquigarrow H + R_1 && G_2(H)\\
H + (C_2H_4)_n &\rightarrow H_2 + R_2 && k_1\\
(C_2D_4)_n &\rightsquigarrow D + R_3 && G_2(D)\\
D + (C_2D_4)_n &\rightarrow D_2 + R_4 && k_2\\
D + (C_2H_4)_n &\rightarrow HD + R_5 && k_3\\
H + (C_2D_4)_n &\rightarrow HD + R_6 && k_4
\end{aligned}$$

Here G_1(H) and G_1(D) are the radiation yields of H_2 and D_2 formed by the molecular route; G_2(H) and G_2(D) are the radiation yields of the processes of formation of H and D atoms; k_1, k_2, k_3, k_4 are the rate constants of reactions of hydrogen atoms with polyethylene molecules, accompanied by abstraction of hydrogen atoms. According to this scheme it is possible to calculate the dependence of the radiation yields of H_2—$G(H_2)$—and D_2—$G(D_2)$—on the fraction of $(C_2H_4)_n$ and $(C_2D_4)_n$ in the mixture. For the case of a dilute solution of $(C_2H_4)_n$ in $(C_2D_4)_n$, the calculation gives

Fig. 1

Figure 1: Fig. 1

$$\frac{G(\mathrm{H}_2)}{F_1} = G_1(\mathrm{H}) + \frac{k_1}{k_4} G_2(\mathrm{H}) F_1, \qquad F_1 = \frac{C_H}{C_D}, \tag{A}$$

and for a solution of $(\mathrm{C_2D_4})_n$ in $(\mathrm{C_2H_4})_n$

$$\frac{G(\mathrm{D}_2)}{F_2} = G_1(\mathrm{D}) + \frac{k_2}{k_3} G_2(\mathrm{D}) F_2, \qquad F_2 = \frac{C_D}{C_H}. \tag{B}$$

By plotting $G(\mathrm{H}_2)/F_1$ against F_1 and $G(\mathrm{D}_2)/F_2$ against F_2 for the radiolysis of solutions of the corresponding composition, we obtain the values of $G_1(\mathrm{H})$ and $G_1(\mathrm{D})$.

In experiments to determine the molecular yields of H_2 and D_2 at a temperature of 30°, mixtures corresponding to the following values of F were used: $F_1 = 3.76;\ 5.65;\ 8.86;\ 9.35;\ 11.5 \cdot 10^{-2}$; $F_2 = 1.58;\ 5.97;\ 9.60;\ 14.7 \cdot 10^{-2}$. The dependences of $G(\mathrm{H}_2)/F_1$ on F_1 and of $G(\mathrm{D}_2)/F_2$ on F_2 for these mixtures are shown in Fig. 1. As is seen from the graphs, the value $G_1(\mathrm{D}) = 0.37 \pm 0.05$, and within the experimental error it does not depend on the dose in the interval 10-60 Mrad; $G_1(\mathrm{H}) = 2.6 \pm 0.4$ at a dose of 10 Mrad; 2.3 ± 0.4 at a preirradiation dose of 20 Mrad, and 2.1 ± 0.4 at a preirradiation dose of 50 Mrad.

The value of $G_1(\mathrm{H})$ may turn out to be smaller than the values given by approximately 10%, since the deuteropolyethylene used contained 2% H atoms. The ratio $[\mathrm{HD}]/[\mathrm{D}_2]$ in the hydrogen formed during radiolysis of pure $(\mathrm{C_2D_4})_n$ is equal to 0.10. The radiation yields of H_2 and D_2 in the radiolysis of pure $(\mathrm{C_2H_4})_n$ and $(\mathrm{C_2D_4})_n$ are, respectively, 6.0 and 3.8; from this one can calculate the fraction of the molecular route in hydrogen formation. It is $10 \pm 1.5\%$ for D_2 and $38 \pm 10\%$ for H_2. The different slopes of the straight lines

in Fig. 1 at different values of the dose of preliminary irradiation of the sample can be explained by the fact that, upon irradiation of polyethylene, acceptors of atomic hydrogen accumulate (free radicals and molecules with double bonds ([1,3])); when hydrogen atoms add to them, they cannot participate in hydrogen-formation reactions. This may be evidenced by the fact that the magnitude of the radiation yield of hydrogen in the radiolysis of pure polyethylene and deuteropolyethylene decreases with increasing dose (see Fig. 2).

Fig. 1. **A**—dependence of the ratio $G(\mathrm{H}_2)/F_1$ on F_1 in the mixture $(\mathrm{C_2H_4})_n$ and $(\mathrm{C_2D_4})_n$. **B**—dependence of the ratio $G(\mathrm{D}_2)/F_2$ on F_2 in the mixture $(\mathrm{C_2H_4})_n$ and $(\mathrm{C_2D_4})_n$. *a*—values of $G(\mathrm{H}_2)/F_1$ for an irradiation dose of 10 Mrad; *b*—20 Mrad; *v*—50 Mrad. The value of G is expressed in units of "number of molecules formed upon absorption of 100 eV of energy."

Fig. 2. Dependence of the radiation yields $G(\mathrm{H_2})$ (1) and $G(\mathrm{D_2})$ (2) on the irradiation dose (Mrad) in the radiolysis of pure polyethylene and deuteropolyethylene

Figure 2: Fig. 2. Dependence of the radiation yields $G(\mathrm{H_2})$ (1) and $G(\mathrm{D_2})$ (2) on the irradiation dose (Mrad) in the radiolysis of pure polyethylene and deuteropolyethylene

Taking into account reactions of atomic hydrogen with free radicals and double bonds leads to the result that, in equations (A) and (B), the second terms will have the form:

$$G_2(\mathrm{H})F_1 \frac{k_1}{k_4 + k_{\mathrm{rad}} \dfrac{C_R}{C_D} + k_{\mathrm{olef}} \dfrac{C_{\mathrm{olef}}}{C_D}},$$

$$G_2(\mathrm{D})F_2 \frac{k_2}{k_3 + k'_{\mathrm{rad}} \dfrac{C_R}{C_H} + k'_{\mathrm{olef}} \dfrac{C_{\mathrm{olef}}}{C_H}},$$

where k_{rad}, k_{olef}, k'_{rad}, k'_{olef} are the rate constants of the reactions

$$\begin{aligned} \mathrm{H} + \mathrm{R} &\to \mathrm{RH} & k_{\mathrm{rad}} \\ \mathrm{H} + \text{olefin} &\to \mathrm{R} & k_{\mathrm{olef}} \\ \mathrm{D} + \mathrm{R} &\to \mathrm{RD} & k'_{\mathrm{rad}} \\ \mathrm{D} + \text{olefin} &\to \mathrm{R}' & k'_{\mathrm{olef}} \end{aligned}$$

C_R and C_{olef} are the concentrations of free radicals and unsaturated molecules, respectively. Thus, with increasing dose, as the⋯

concentrations of olefins and free radicals, the slope of the straight lines in plots of $G(\mathrm{H_2})/F_1$ versus F_1 and $G(\mathrm{D_2})/F_2$ versus F_2 should decrease. As is seen from Fig. 1, such a decrease in the slope with increasing dose does indeed occur in the case of polyethylene. In the case of deuteropolyethylene this dependence is apparently weaker.

Knowing the values $G_1(\mathrm{H})$ and $G_1(\mathrm{D})$ and the radiation yields of $\mathrm{H_2}$ and $\mathrm{D_2}$ in the radiolysis of pure $(\mathrm{C_2H_4})_n$ and $(\mathrm{C_2D_4})_n$, one can calculate the radiation yields of $\mathrm{H_2}$ and $\mathrm{D_2}$ formed by the radical pathway. At a dose of 10 Mrad these values are:

Fig. 2. Dependence of the radiation yields $G(\mathrm{H_2})$ (1) and $G(\mathrm{D_2})$ (2) on the irradiation dose (Mrad) in the radiolysis of pure polyethylene and deuteropolyethylene

$$G_2(\mathrm{H}) = 6.0 - 2.6 = 3.4, \qquad G_2(\mathrm{D}) = 3.8 - 0.37 = 3.43.$$

The values G_2(H) and G_2(D) agree with good accuracy. Thus, the source of the isotope effect in the reactions of radiolytic formation of hydrogen from polyethylene is the reaction of molecular elimination of hydrogen.

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