PHYSICAL CHEMISTRY

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1963

SovietRxiv

Abstract

Full Text

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KINETICS OF GAS EVOLUTION IN THE LOW-TEMPERATURE RADIOLYSIS OF PARAFFIN AND POLYETHYLENE

(Presented by Academician N. N. Semenov, May 9, 1963)

A considerable fraction of the hydrogen formed in the radiolysis of solid paraffin or polyethylene, which is the principal gaseous product of radiolysis at a temperature close to the boiling point of nitrogen, does not enter the gas phase, remaining trapped in the solid substance (1). When the samples are warmed after irradiation has ceased, hydrogen begins to be released from the solid hydrocarbon into the gas phase. It should be assumed that what is trapped in the substance is precisely molecular, and not atomic, hydrogen, since electron paramagnetic resonance spectra do not reveal the presence of hydrogen atoms in polyethylene (or paraffin) irradiated at the temperature of liquid nitrogen (2).

The present work is devoted to elucidating the nature of the trapping of hydrogen in irradiated paraffin and polyethylene, determining the largest amounts of hydrogen that can be retained in this way, and studying the kinetics of gas evolution from radiolyzed samples after irradiation has ceased. The trapping of hydrogen is, in all probability, associated with the retardation of H_2 diffusion at low temperature and can occur both in a radiolyzed hydrocarbon and in a hydrocarbon not subjected to the action of ionizing radiation.

As objects of study we selected paraffin with a melting point of 52–55° and high-pressure polyethylene. A sample in the form of a plate 0.1–0.8 mm thick and weighing 0.03–0.2 g was sealed into a copper cup and placed in a glass ampoule, which was attached to the outlet flange of the electron accelerator of the Institute of Chemical Physics, Academy of Sciences of the USSR. The electron energy was 1.6 MeV. The temperature of the sample was measured with a thermocouple sealed into its surface. The lower part of the ampoule, in which the sample was located, was immersed in a Dewar vessel with liquid nitrogen. Before irradiation began, the ampoule was evacuated with a forevacuum pump to a pressure of about 10^{-2} mm Hg. The pressure of the evolved gas was measured by means of a U-shaped manometer, in which D-4 grade oil served as the working liquid. The manometer readings were recorded remotely with the aid of an industrial television installation, PTU-2.

In addition, experiments were carried out in which the amount of hydrogen formed during the radiolysis of polyethylene was continuously measured from the intensity of the line $m/e = 2$ (the H_2^+ ion) in the mass spectrum of the gaseous radiolysis products. These measurements were made with the aid of a mass spectrometer placed under the beam of fast electrons. The dose absorbed by the sample was calculated from the current of electrons that had passed through the sample and from the stopping power of the hydrocarbon.

The curves describing the observed kinetics of hydrogen evolution during the radiolysis of paraffin and polyethylene (at a temperature of about 100° K) are presented in Fig. 1 (curves 1, 2, 4). In the same figure, for comparison, the initial portion of the kinetic curve for hydrogen formation during the radiolysis of paraffin is given (^{3}). It is evident that the initial portions of the curves of the observed kinetics of hydrogen evolution have a much smaller slope than the slope of curve 3. As the dose increases, the slope increases and reaches a limiting value corresponding to the radiation yield of hydrogen formation from paraffin (dose about $150 \cdot 10^{20}$ eV/g).

For polyethylene, the slope of the curve does not increase up to a dose of 2000 Mrad, and then begins to rise slowly; moreover, in the interval 4550–6250 Mrad the apparent radiation yield of hydrogen evolution (0.21)

under the conditions of the experimental geometry, is still about 2 times less than the radiation yield of hydrogen formation (0.48) at a dose rate of about 7 Mrad/min.

The kinetics of gas evolution from radiolyzed samples containing retained hydrogen was also studied when they were heated to various temperatures. In this case the samples were kept at constant temperature values (above the temperature of liquid nitrogen) by cooling the ampoule with a jet of cold gaseous nitrogen. The experimental data on the kinetics of gas evolution from radiolyzed samples were treated using an approximate solution of the corresponding diffusion equation, which has the following form:

$$\ln\left[1 - \frac{Q(t)}{Q_0}\right] = -\frac{\pi^2 D}{4l^2}t,$$

where $Q(t)$ is the amount of hydrogen released by time t, Q_0 is the total amount of retained hydrogen, D is the diffusion coefficient of hydrogen, and l is the half-thickness of the sample.

Fig. 1. Evolution of hydrogen into the gas phase during low-temperature (-175°) radiolysis of paraffin and polyethylene. 1—radiolysis of paraffin, dose rate $3.2 \cdot 10^{20}$ eV/g • min; 2—the same at a dose rate of $2.16 \cdot 10^{20}$ eV/g • min; 3—initial section of the dependence of the amount of hydrogen formed on dose during radiolysis of paraffin; 4—radiolysis of polyethylene, dose rate $3 \cdot 10^{20}$ eV/g • min.

The dependence of the quantity $-\ln\alpha = -\ln\frac{\pi^2 D}{4l^2}$ on the reciprocal temperature of a paraffin sample is shown in Fig. 2. It is seen that the temperature dependence of α (and hence also of the formal diffusion coefficient D) is described by the Arrhenius equation with an activation energy $E = 3.4 \pm 0.5$ kcal/mol. In addition, it was found that the value of D determined in this way increases with irradiation dose up to a dose of about $150 \cdot 10^{20}$ eV/g; at this dose the limiting value of D is reached. This change in D with dose is apparently associated with changes in the structure of the paraffin sample during radiolysis (the appearance of pores, microcracks, etc.).

Fig. 2. Dependence of $-\ln\alpha$ (α is a quantity proportional to the diffusion coefficient of hydrogen) on reciprocal temperature, determined in experiments on low-temperature radiolysis of paraffin. At various temperatures the rate of hydrogen evolution was measured from samples irradiated with different doses. 1—dose $16 \cdot 10^{20}$ eV/g; 2—dose $40 \cdot 10^{20}$ eV/g; 3—doses $176 \cdot 10^{20}$ and $306 \cdot 10^{20}$ eV/g.

We note that for the temperature dependence of the rate of gas evolution from irradiated polyethylene, we were unable to obtain an Arrhenius dependence. Possibly this is connected with a continuous change in the structure of the sample during heating as a result of recombination of radicals and the formation of "crosslinks." When the sample is heated, the greatest amount of gas is released in the range 160-190°K, which is in agreement with the results of Dole et al. (^{1}).

The results concerning the amounts of hydrogen retained in samples of paraffin and polyethylene irradiated at low temperature are the most interesting from our point of view. When the samples were warmed,

of irradiated paraffin (dose above 250 Mrad) hydrogen is released; the ratio V of its volume under normal conditions (in cm^3) to the initial weight of the sample (in grams) is approximately 10 ($V \simeq 10$). For polyethylene that received a dose of 2000 Mrad, $V = 100$; for samples that received a dose of 4550 Mrad, $V = 260$; for 6250 Mrad, $V \simeq 285$.

We carried out special experiments in order to clarify what amounts of hydrogen can be retained in polyethylene if the polyethylene is "saturated" with hydrogen at high pressure. In these experiments polyethylene was heated to its softening temperature under a hydrogen pressure of 1-150 atm. The polyethylene was then cooled with liquid nitrogen, and the hydrogen was pumped out of the gas phase. Hydrogen could remain retained in the polyethylene for several hours without signs of its release into the gas phase. The dependence obtained for V on the hydrogen pressure P is linear; at $P = 150$ atm the value of V reaches 3.8. To obtain the greatest value of V observed in the radiolysis of polyethylene at a dose of 6250 Mrad, a hydrogen pressure of about 9300 atm would be required, if one assumes that extrapolation of the linear dependence of V on P to the region of large P is justified. It is possible that the retention of hydrogen during the radiolysis of polyethylene is connected with the accumulation of H_2 molecules at the sites where double bonds are formed, which have a smaller "molecular volume." The retention of hydrogen in radiolyzed hydrocarbons is predominantly diffusional in character and is not due, for example, to equilibrium solubility of hydrogen. Apparently, one can also exclude any "chemical" mechanism of hydrogen retention associated, for example, with the formation at low temperature of stabilized intermediate compounds capable of decomposing upon heating with formation of hydrogen. In fact, the radiolysis of paraffin and polyethylene leads to the formation of analogous products (hydrogen, free radicals of the alkyl and allyl type, molecules with double bonds of the trans-vinylene type), and the radiation yields of these products are close. Meanwhile the maximum values of V for paraffin and polyethylene differ sharply: for paraffin the limiting value is $V = 10$, whereas for polyethylene V can reach 285. Such a large difference between these values may be connected with the different "rigidity" of these substances at the temperature of liquid nitrogen. For a polymer consisting of large molecules, it is natural to expect greater rigidity than for paraffin, which consists of comparatively small molecules. We note that hydrogen retention takes place in an amorphous substance, since at doses above 1000 Mrad the crystalline phase in polyethylene disappears completely[3]. It is interesting that hydrogen retained in radiolyzed polyethylene samples is released at a low rate when irradiation is stopped. If it is assumed that the dependence of the amount of released hydrogen N on time t is described by the equation

$$N = SC\sqrt{\frac{D}{\pi}}\,t^{1/2},$$

where C is the concentration of hydrogen retained in the sample, S is the surface area of the sample, and D is the diffusion coefficient, then the diffusion coefficient D determined from the observed rate of hydrogen release will be $2.2 \cdot 10^{-13}$ $\mathrm{cm}^2/\mathrm{sec}$ and $1.2 \cdot 10^{-12}$ $\mathrm{cm}^2/\mathrm{sec}$ for samples that received doses of 4550 and 6250 Mrad, respectively. The order of magnitude of the time τ for hydrogen to escape from the sample can be estimated by the formula

$$\tau = \frac{l^2}{2D},$$

where l is the half-thickness of the sample, equal to $1 \cdot 10^{-2}$ cm. Then $\tau = 2 \cdot 10^8$ $-4 \cdot 10^7$ sec. The difference in τ for samples that received different doses may be explained by their different structure.

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Received
26 IV 1963

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