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Abstract

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FORMATION OF HD IN THE REACTION OF HYDROGEN ATOMS FORMED IN THE GAS PHASE WITH SOLID DEUTEROPOLYETHYLENE

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The question of the possibility of a reaction of the type

$$H + M \rightarrow H_2 + R, \tag{1}$$

where M is a hydrocarbon molecule and R is a free radical, in solid hydrocarbons is a very important one, since this reaction, along with the recombination reaction

$$H + H \rightarrow H_2, \tag{2}$$

is invoked to explain the formation of hydrogen during the radiolysis of hydrocarbons. The experimental detection of reaction (1) in radiolysis processes in the solid phase is associated with considerable difficulties and, as far as the authors know, direct evidence of its occurrence has so far been obtained by no one. Sometimes, in interpreting data on the values of $G(H_2)$ in various hydrocarbons, it is assumed that reaction (1) can be carried out predominantly by "hot" H atoms. In this connection, special importance attaches to experiments aimed at the direct detection of reaction (1) for the case of "thermal" H atoms. Experimentally, the most direct approach consists in studying the action of a stream of H atoms, formed in the gas phase, on the surface of solid polyethylene. In this case reaction (1) could be detected by studying the formation of HD in the reaction of D atoms with ordinary polyethylene or of H atoms with deuteropolyethylene. This method was used by us in the present work. The basic principles of the technique were developed by Klein and Scheer [1,2] and by Ponomarev and Tal' roze [3,4], who applied it in studying reactions of hydrogen atoms with unsaturated compounds in the solid state. However, the application of such a technique in the case of saturated compounds is associated with considerable difficulties, since process (1) is *a priori* much slower than the reactions of addition of H atoms to simple unsaturated compounds. Therefore the role of various "background" reactions sharply increases. For example, the formation of HD can occur not only in a reaction of type (1), but also in the interaction of D atoms with H_2O molecules, some amount of which is always adsorbed on the walls of the apparatus, and with –OH groups present on the surface of the glass. Therefore, in particular, we were able to apply only the variant of the method in which the exchange of light hydrogen with deuteropolyethylene was studied, and not the action with ordinary polyethylene.

Another difficulty consisted in obtaining a high vacuum in a closed reaction vessel containing polyethylene. Indeed, although the vapor pressure released from polyethylene at 25°C is $3 \cdot 10^{-8}$ mm Hg, it increases rapidly with rising temperature; the corresponding activation energy for the evolution of dissolved hydrocarbon gases is 9 kcal/mole [5]. At temperatures around 300°C, the process of thermal decomposition of polyethylene molecules, yielding hydrocarbon gases [6], becomes noticeable.

We had to exclude the presence of gas-evolution and pyrolysis products in the gas phase, since they can subsequently decompose on the go-

the hot tungsten filament, or else to react with atomic hydrogen in the gas phase, leading to uncontrolled experimental errors. To overcome these difficulties, it proved necessary to develop an experimental procedure more advanced than those described.

The scheme of the experimental apparatus is shown in Fig. 1. The reaction vessel consists of two parts. In one part of the apparatus (1) there is placed

Fig. 1. Scheme of the experimental apparatus.
1 –vessel in which hydrogen atoms were generated, *2* –vessel with the sample under study, *3* –tungsten spiral, *4* –sample, *5* –cup for placing the sample, *6* –glass tube–jacket, *7* –electric heater made of nichrome wire, *8* –thermocouple, *9* –ground joint, *10* –thermocouple leads, *11* –heater leads, *12* –Dewar vessel, *13* –ground joint for taking gas samples, *14* –ground joint to the gas admission and pumping system, *15* –thermocouple vacuum-gauge tube, *16* –liquid-nitrogen level.

a tungsten filament (3), on which dissociation of H_2 molecules occurs; in the other part (2) there is a sample of solid deuteropolyethylene (4). Powdered deuteropolyethylene (powder weight 0.02-0.04 g) was placed in a glass cup (5). An electric heater made of nichrome wire was wound around the outside of this cup, with the aid of which the temperature of the powder could be varied over wide limits. The temperature of the cup walls, equal to the temperature of the powder, was measured by means of a copper-constantan thermocouple and was kept constant with an accuracy of ±2-3°C. The entire reaction vessel was immersed in a Dewar vessel with liquid nitrogen. This was necessary in order to freeze out hydrocarbon products released from the polyethylene when it was heated to 150-200°C. The isotopic composition of the hydrogen was determined with an MX-1302 mass spectrometer.

The experiments were carried out with samples of deuteropolyethylene of two types, differing in degree of isotopic purity (98 and 94% of the D isotope). Samples irradiated at a temperature of ~ 300°K with electrons of energy 1.6 MeV in vacuum or in an air atmosphere were also investigated. Before opening the ampoules in which the irradiation in vacuum had been carried out, they were heated at a temperature of about 100°C for several hours, thereby destroying free radicals stabilized in the irradiated polyethylene (^{7}). Study of the kinetics of HD formation showed that the yield of HD is, with sufficient accuracy, proportional to the reaction time. Therefore, subsequently, as a relative measure of the rate of the HD-formation reaction, V, we used the value of the ratio HD/H_2, recalculated to an exposure time of 5 min (in the experiments the exposure times ranged from 30 sec at high temperature to 5-10 min at temperatures below 0°C). Special experiments showed that HD formation takes place in the polyethylene, and not in the gas phase, and also not on the walls of the reaction vessel or on the surface of the tungsten filament (in these experiments the surface of the cup was covered with metal foil, which destroyed H atoms near the polyethylene surface but did not prevent gases from leaving the polyethylene and entering the volume of the reaction vessel).

Data on the temperature dependence of the rate of HD formation in the reaction of H atoms with deuteropolyethylene containing 98% D atoms are presented in Fig. 2 in the form of the dependence of $\lg V$ on $1/T$. It is seen that in the range from $-196°$ to $-100°$ the value of V does not depend on temperature, while in the range from $-100°$ to $+110°$ it is satisfactorily described by the Arrhenius equation with

with an activation energy corresponding to 2-3 kcal/mole. The independence of V from temperature in the region below $-100°$, as shown in special experiments, is explained by the formation of HD on the walls of the reaction vessel during the interaction of H atoms with frozen hydrocarbon gases. The measured activation energy for HD formation may not be the activation energy of the reaction associated with attack by an H atom on the main chain $\sim CD_2—CD_2 \sim$. It is known

[Figure 2]

Fig. 2. Dependence of $\lg V \left(\lg \frac{HD}{H_2}\right)$ on $1/T$.

I—experiment with unirradiated deuteropolyethylene (98% at. D), *II*—experiment with deuteropolyethylene (98% at. D) irradiated in vacuum with a dose of 240 Mrad. (the rate of generation of H atoms was reduced; the crosses on curve *I* correspond to the usual rate of generation of H atoms), *III*—experiment with deuteropolyethylene (98% at. D) irradiated in air with a dose of 120 Mrad. *IV*—experiment with deuteropolyethylene irradiated in vacuum with a dose of 100 Mrad.

that polyethylene also contains some number of molecules with double bonds of the trans-vinylene, vinyl, and vinylidene branching types, and also, possibly, a small number of oxygen-containing molecules. In order to determine whether the observed isotopic exchange is connected with the presence of all these "impurities" in deuteropolyethylene, we carried out experiments to study the rate of HD formation in the reaction of H atoms with irradiated samples of deuteropolyethylene. It is known that during the radiolysis of polyethylene the concentration of double bonds of the vinyl and vinylidene types slowly increases, while the concentration of double bonds of the trans-vinylene type and of tertiary carbon atoms (in cross-links) increases much more rapidly ([8]). We used samples of deuteropolyethylene irradiated in vacuum with doses of ~ 100 and ~ 240 Mrad. As a study of the infrared absorption spectra of samples of radiolyzed deuteropolyethylene showed, these doses correspond to an increase in the concentration of double bonds of the trans-vinylene type by ~ 4 and ~ 10 times, respectively. In addition, as a result of cross-link formation, the concentration of tertiary carbon atoms increases by several orders of magnitude. If the observed formation of HD were due to an exchange reaction with molecules containing double bonds or tertiary carbon atoms, then the rate of HD formation would increase for irradiated deuteropolyethylene samples by at least 4 or, correspondingly, 10 times. However, no substantial changes either in the activation energy or in the absolute value of V were found (see Fig. 2, straight lines II and IV). We note that the use of radiolyzed and, consequently, cross-linked deuteropolyethylene samples allowed us to extend the investigated temperature range to 200°C, with the sample not melting and remaining powdery throughout. The plot of $\lg V \div 1/T$ in the region of higher temperatures remained linear throughout, without signs of any break that could be ascribed to the appearance of a contribution from a reaction proceeding with a higher activation energy (for example, if the activation energy of 2–3 kcal/mole corresponded to the reaction of H atoms with double bonds or, in general, with any "impurities," then at high temperature one might expect the predominance of HD formation by a reaction of type (1), proceeding with participation of the main mass of the polymer). Measurements were also carried out on the sample that had received a dose of 240 Mrad, in which we attempted to detect a correlation between the rate of HD formation and the rate of possible hydrogen uptake as a result of hydrogenation of double bonds by atomic hydrogen.

It turned out that although the rate of HD formation at a temperature of 115° exceeds the corresponding rate at liquid-nitrogen temperature by approximately 2 orders of magnitude, the rate of hydrogen uptake in the apparatus, recorded from the readings of a thermocouple vacuum gauge, is the same at both temperatures and is, in all probability, associated with adsorption of H atoms on the cold glass walls of the apparatus. On the basis of the experimental results obtained, i.e., 1) constancy of the value of V for irradiated and unirradiated samples, 2) absence of breaks in the plot of $\lg V$ vs. $1/T$ at high temperature, 3) absence of appreciable uptake of hydrogen by polyethylene containing double bonds, it may be asserted that the activation energy found is not associated with a reaction involving double bonds. Results 1) and 2) also make it possible to exclude the possible participation of molecules with tertiary carbon atoms. In addition to experiments with samples irradiated in vacuum, an experiment was carried out with samples irradiated in air with a dose of about 120 Mrad. It is known that in this case oxygen-containing compounds (with carbonyl and ether groups (^{8})) are formed both on the surface of the polyethylene and in the bulk. The experimental results presented in Fig. 2 show that no substantial increase in the rate of HD formation occurs. The course of the plots of $\lg V$ vs. $1/T$ (at temperatures below 35°C) coincides with the form of the plots for samples irradiated in vacuum and for unirradiated samples. However, at a temperature of 35°C a break is observed in the plot, and the subsequent slope of the straight line corresponds to an activation energy of 4.3 kcal/mole. Since in this case as well no substantial change in the value of V is observed, we arrived at the conclusion that none of the possible "impurities" in deuteropolyethylene participates in the HD-formation reaction and that the activation energy found corresponds to reaction (1). Thus it has been shown that in solid polyethylene a reaction of type (1) can indeed occur under the action of thermal H atoms on the polymer.

The measured value of the activation energy is, of course, not the true activation energy E of process (1), but represents a certain effective value E . The value E is determined (^{9}) not only by the value of E, but also by the activation energy of diffusion of atomic hydrogen E_D and its heat of solution E_p in solid deuteropolyethylene. The corresponding expressions for E are as follows:

$$E = \frac{E + E_D}{2} - E_p$$

(for the case when the principal mechanism of hydrogen loss in solid deuteropolyethylene is reaction (1)) and

$$E = E + \frac{E_D}{2} - E_p$$

(for the case when atomic hydrogen in solid deuteropolyethylene is lost by recombination (2)). If one assumes that $E = 6$–7 kcal/mole, $E_D = 7$–9 kcal/mole (the activation energy for diffusion of He atoms in ordinary polyethylene), and $E_p = 3$–4 kcal/mole, then, according to the first equation, reasonable agreement with the value of E is obtained.

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