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Abstract

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EFFECT OF Co^{60} γ-RADIATION ON ISOTOPIC EXCHANGE BETWEEN HYDROCARBON POLYMERS AND GASEOUS DEUTERIUM

(Presented by Academician V. A. Kargin, 12 XII 1960)

In work (^{1}) it was shown that, under the action of ionizing radiation, isotopic exchange of hydrogen is observed between certain polymers and gaseous deuterium. It is known that this process, which does not occur in the absence of radiation, was explained by the fact that the decomposition of polymer molecules into radicals and hydrogen atoms under the action of radiation is reversible to some extent, as a result of which deuterium atoms are incorporated into polymer molecules. In work (^{1}), the active zone of a water–water reactor was used as the radiation source; the experiments were carried out in sealed glass ampoules at a deuterium pressure close to atmospheric.

The aim of the present work was a more detailed study of the indicated phenomenon using pure Co^{60} γ-radiation, and also an investigation of the possibility of exchange between certain liquid hydrocarbons (*n*-pentane, cyclopentane, *n*-hexane, cyclohexane, and benzene) and gaseous deuterium under the action of Co^{60} γ-radiation, since such exchange reactions, like reactions with hydrocarbon polymers, are known not to proceed under ordinary conditions in the absence of radiation. As a first approximation, we studied the dependence of the observed effect on the magnitude of the polymer surface, on the radiation dose, on the deuterium pressure, and on temperature.

Method. The experiments were carried out in metal ampoules at deuterium pressures up to 150 atm. A weighed portion of the sample under study (0.3–0.5 g) was placed in a hermetically sealed ampoule of approximately 20 ml capacity, equipped with a valve. The ampoule was evacuated and filled with gaseous deuterium ($\sim$ 99.6% D) from a cylinder in which the pressure exceeded 150 atm. The gaskets and valve seals were made of polyethylene. The pressure was monitored with a calibrated standard manometer connected to the filling system. After filling, the ampoule was disconnected and the valve was closed with a special cap with a plug to prevent possible leakage of deuterium through the valve as a result of the action of radiation on the seal. The ampoules thus prepared were irradiated in a Co^{60} γ-radiation source. After irradiation, the deuterium pressure in the ampoule was checked, the sample under study was removed, and its deuterium content was determined.

For this purpose, a weighed portion (~ 0.15 g) was burned in an oxygen atmosphere at 900°, the water from combustion was collected, purified from possible contaminants and CO_2 admixture by distillation in vacuum with addition of BaO, and the deuterium concentration in it was determined by the drop method ([2]). The accuracy of the isotopic analysis was $\pm 0.02\%$. The value obtained corresponded to the average deuterium content in the substance. Control experiments showed that

prolonged contact of the polymer with gaseous deuterium in the absence of irradiation does not lead to an increase in the weight of the water from combustion of the polymer. This indicates that the presence of deuterium in the polymer in irradiation experiments is not connected with adsorption of hydrogen on the surface of the film, but is due to the incorporation of deuterium into the molecules of the substance under study.

Results and discussion. To test the effect of pure γ-radiation from Co^{60}, isotopic exchange was studied between gaseous deuterium, on the one hand, and two polymers—polyethylene and polymethyl methacrylate—on the other. Of the polymers investigated in [1],

Fig. 1 Fig. 2

Fig. 1 **Fig. 2**

maximum exchange is observed in the case of polyethylene, whereas for polymethyl methacrylate the fraction of exchange is minimal. In both experiments the dose was 400 million r; the deuterium pressure was 150 atm. With polymer samples of about 1 g and ampoule volumes of 70 ml, the deuterium concentration was 0.55 at.% in the case of polyethylene and 0.27 at.% in the case of polymethyl methacrylate. These data show that the type of ionizing radiation does not exert a substantial influence on the hydrogen-exchange reaction studied. The absence of noticeable deuterium incorporation into polymethyl methacrylate in [1] was probably associated with an insufficient radiation dose.

As the experiment shows, the amount of incorporated deuterium depends strongly on the magnitude of the polyethylene surface area. Thus, at a dose of 200 million r and a deuterium pressure of 150 atm, the deuterium concentration in the case of a polyethylene film 0.3 mm thick was 0.45 at.%, whereas in an experiment with powdered polyethylene the deuterium concentration was 1.55 at.%. The main characteristics of the process were studied using unstabilized polyethylene in the form of a film 0.07–0.08 mm thick.

The results of studying the dependence of the concentration of deuterium incorporated into the polymer on the integral radiation dose are given in Fig. 1. The curve characterizes the increase in the deuterium concentration in the sample as a function of dose. The dependence of the deuterium concentration in polyethylene on the deuterium pressure in the ampoule was studied at a radiation dose of 200 million r. The corresponding data are given in Fig. 2. They show that within the range from 2 to 140 atm the deuterium concentration increases only by a factor of 2–2.5. It is obvious that at a deuterium pressure close to zero, exchange cannot take place. Therefore, for the pressure region below 2 atm, the experimental curve was extrapolated in the form of the dashed line shown in Fig. 2.

Thus, a characteristic feature of the process under study is the rapid increase in the deuterium concentration in the polymer with increasing deuterium pressure in the low-pressure region (up to 2 atm) and a comparatively slow increase in the higher-pressure region (up to 150 atm).

To clarify the dependence of the observed effect on temperature, in addition to experiments at room temperature, experiments were also carried out at 100° (boiling water) and -196° (liquid nitrogen). The radiation dose in both experiments was 80 million r, and the deuterium pressure was ~ 100 atm. The deuterium concentration in the polymer in the experiment carried out at $t = 100^\circ$ was 0.25 at.%, and at $t = -196^\circ$, 0.08 at.%.

Table 1

Isotopic exchange of hydrogen between hydrocarbons and gaseous deuterium under the action of γ-radiation from Co^{60}

Substance	Hydrocarbon sample, g	Deuterium pressure, atm before irradiation	Deuterium pressure, atm after irradiation	Deuterium concentration, at. %	Yield, molecules per 100 eV	Substance	Hydrocarbon sample, g	Deuterium pressure, atm before irradiation	Deuterium pressure, atm after irradiation	Deuterium concentration, at. %	Yield, molecules per 100 eV
n-Pentane	0.80	10	10	0.09	0.8	*n*-Hexane	0.55	142	135	0.26	2.2
n-Pentane	0.70	147	141	0.46	3.9	Cyclohexane	0.43	10	10	0.02	0.1
Cyclopentane	0.50	10	10	0.18	1.3	Cyclohexane	0.50	142	142	0.21	1.6
Cyclopentane	0.70	147	125	0.55	4.0	Benzene	0.80	10	10	0.05	0.2
n-Hexane	0.46	10	10	0.10	0.8	Benzene	0.55	147	141	1.32	5.2

The results of experiments on isotopic exchange between several liquid low-molecular-weight hydrocarbons and gaseous deuterium are given in Table 1.

The data obtained indicate that, at a dose of 200 million r and a deuterium pressure of 10 atm, deuterium from the gas phase is incorporated into the CH bonds of the hydrocarbons studied.*

Increasing the pressure to ∼ 145 atm leads in all cases to a significant increase in the deuterium concentration in the hydrocarbon.

Thus, the previously discovered effect of initiation of isotopic hydrogen exchange between the C—H bonds of certain polymers and gaseous deuterium under the action of ionizing radiation has been confirmed. It has been shown that the type of radiation has no noticeable effect on the observed exchange process and that such exchange is characteristic not only of high-molecular-weight compounds, but also of low-molecular-weight hydrocarbons. The dependences of the fraction of exchange on temperature and deuterium pressure have been studied for hydrocarbons of different structure.

The results obtained shed light on the mechanism of isotopic exchange in the case of the use of radioactive isotopes (for example, tritium), in which the isotope' s own radioactivity, analogously to external radiation, may serve as a factor initiating exchange.

The observed effect should be taken into account when radioactive indicators are used in chemistry and biology, where the activation energies of exchange reactions may be sufficiently low, and the values obtained when using stable and radioactive isotopes of one and the same element may lead to different results.

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* The hydrocarbons were identified by boiling point, which did not change during the irradiation process.

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

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