FORMATION OF POLYMER PRODUCTS IN THE RADIOLYSIS OF MIXTURES OF HEXAFLUOROBENZENE WITH PERFLUOROCYCLOHEXANE AND PERFLUORONONANE

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UDC 541.15:678.7

The dependence of the formation of polymer products in the (n, \( \gamma \))-irradiation of mixtures of hexafluorobenzene with perfluorocyclohexane and n-perfluorononane upon the concentration of hexafluorobenzene was determined. A hypothesis was formulated on the inhibiting effect of hexafluorobenzenes in the radiolysis of perfluorocyclohexane. It was established that in the radiolysis of n-perfluorononane, hexafluorobenzene plays the role of a polymerization-initiating agent.

The unique properties of organochlorine compounds, for example, their high thermal stability (up to 600°C in perfluorinated polyphenyls [1]) and their chemical inertness, have been responsible for their wide use in the atomic energy industry [2]. Progress in this field sets new requirements for such compounds — requirements of radiation-thermal stability. The combination of sufficiently high radiation-thermal stability of fluorocarbons, which is possessed by perfluorinated polyphenyls [3], with the low neutron absorption cross section of fluorine atoms opens up broad prospects for the use of these compounds in nucleonics. The absence of molecular fluorine as a radiolysis product, as well as the absence of any corrosive action of the other radiolysis products on aluminum [3, 4], once again confirms the possibility of using fluorocarbons.

As is well known, aromatic hydrocarbons exert an inhibiting effect upon the radiolysis of aliphatic hydrocarbons. However, there are no data in the literature on an analogous influence of perfluorinated aromatic compounds on the radiolysis of aliphatic fluorocarbons, in view of which in this work we determined the dependence of the formation of high-boiling products ("polymer") on the concentration of hexafluorobenzene in (n, \( \gamma \))-irradiation of its mixtures with perfluorocyclohexane and n-perfluorononane. The radiolysis of such mixtures is interesting from the standpoint of the protective action of aromatic compounds in various compositions. Irradiation was conducted in molybdenum glass ampoules.
Since a large error in the concentration of hexafluorobenzene might appear in the preparation of the ampoules for irradiation, in the cases of n-perfluorononane, the following specially developed method was used. After degasification by repeated alternation of the processes of freezing and melting under vacuum, the weight of a sample of n-perfluorononane in ampoule 1 (Fig. 1) was determined, considering the weight of the lubricant on the ground joints. Before each operation of filling, degasification of hexafluorobenzene in ampoule 2 was also carried out. After degasification of the cell for the filling, it was sealed off at a residual pressure of ~ 10^-3 mm Hg. Hexafluorobenzene was frozen out in ampoule 1 with liquid nitrogen directly from ampoule 2 or (if the mixtures were prepared with a low hexafluorobenzene concentration), from the tube between stopcocks 3 and 4, filled with vapor, by turning stopcock 3. The amount of hexafluorobenzene vapors in the tube varied depending upon the temperature of ampoule 2.

Irradiation was conducted at ~ 50°C in the water-filled experimental channel of the VVR-2 reactor of I.V. Kurchatov Atomic Energy Institute. The dose of absorbed energy was determined according to calorimetric data in the irradiation of polyterafluoroethylene with a correction of electron density. In the case of mixtures of n-perfluorononane, the dose corresponded to 66 Mrad of energy absorbed by hexafluorobenzene; in the case of perfluorocyclohexane the dose was 50 Mrad.

The polymer radiolysis products were isolated by simple distillation with continuous evacuation (~ 10^-3 mm Hg) through a trap 3, cooled with liquid nitrogen, and connected to ampoule 1 by a flexible vacuum hose 2 (Fig. 2). The inner branch of ampoule 1 was broken with a glass breaker with steel balls inside. The redistillation was conducted at a temperature of 100°C to a constant weight of ampoule 1.

Figures 3 and 4 present the values of the yields of the polymer products as a function of the electronic fraction of hexafluorobenzene in the mixture with n-perfluorononane. At low concentrations, the yield of polymer products (see Fig. 3) is expressed by the number of molecules of n-perfluorononane converted to polymer products with the absorption of 100 eV of energy.

The yields of the polymer products increase as a linear function of the hexafluorobenzene concentration; the calculated content of the polymer in the mixtures (according to the yield in individual components) is lower than the experimental value. This interesting fact is probably associated with the specific properties of organofluorine compounds. In contrast to hydrocarbons, in normal, alicyclic, and aromatic fluorinated compounds, these properties are manifested in approximately identical radiation chemical yields of the polymer products (see Table 1). It should be emphasized that frequently fluorinated aromatic compounds are more inclined to polymerize under the action of ionizing radiations than are perfluorinated saturated fluorocarbons of normal and cyclic structure.