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## Abstract

## Full Text

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# RADIATION SYNTHESIS OF POLYMERS BASED ON TRIMERIC CYCLIC DIMETHYLPHOSPHINOBORINE

Most of the known trimeric cyclic phosphinoborines are distinguished by high hydrolytic and chemical stability and are capable of withstanding heating to 300° and higher. Evidently, among polymeric phosphinoborines, polycyclic structures should be of greatest interest, since linear polymers, as is known from individual examples ([1]), are of low stability and, on heating, undergo destruction with the formation of trimeric and tetrameric rings. It has recently been shown that borazoles, which are close in nature to cyclic phosphinoborines, polymerize under the action of ionizing radiation with the formation of polymeric products of polycyclic structure ([2]). Radiation polymerization of borazoles proceeds by a chain process, in which each act of chain growth is accompanied by the liberation of one molecule of hydrogen or methane. These results make it possible to expect that irradiation may produce an analogous effect also in the case of cyclic phosphinoborines. The most accessible and well-characterized trimeric cyclic dimethylphosphinoborine was chosen as the object of study. Irradiation was carried out on the electron accelerator of the Institute of Physical Chemistry of the Academy of Sciences of the USSR, operating at a voltage of 800 kV. The dose rate was $6.5 \cdot 10^4$ rad/sec. Irradiation was carried out in evacuated, sealed, thin-walled glass ampoules. The irradiation conditions and the results of the experiments performed are given in Table 1.

**Table 1**

**Radiation yield of dimethylphosphinoborine polymers**

| Experiment No. | $t$-ra, °C | Phase state of the monomer | dose rate, $P_m \cdot 10^{-18}$ eV/g | irradiation duration, h | Total yield, wt. % | Total yield, g, mol per 100 eV | Yield insoluble in benzene, wt. % | Yield insoluble in benzene, g, mol per 100 eV | Yield soluble in benzene, wt. % | Yield soluble in benzene, g, mol per 100 eV | Yield of gaseous products, ml | Yield of gaseous products, g, mol per 100 eV |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 90 | Melt | 0.4 | 10 | 26 | 4.9 | 6 | 1.1 | 20 | 3.8 | 18 | 3.3 |
| 2 | 90 | » | 4.0 | 2 | 17 | 1.6 | 5 | 0.5 | 12 | 1.1 | 43 | 3.9 |
| 3 | 90 | » | 4.0 | 13 | 67 | 1.0 | 40 | 0.6 | 27 | 0.4 | 42 | 0.56 |
| 4 | 30 | Crystal | 4.0 | 12 | 44 | 0.7 | 27 | 0.4 | 17 | 0.3 | – | – |

At an irradiation dose of $4 \cdot 10^{18}$ eV/g•sec, about 70% of the initial monomer was converted into polymeric products of two kinds. One of the polymers obtained did not dissolve in benzene or in other ordinary solvents and dissolved only on heating in dimethylformamide and tricresol. It is a white solid substance with a reduced viscosity of 0.14; its molecular weight, determined by the isopiestic method, is 5200. Its thermomechanical properties are presented in Fig. 1. In moist air and after being kept in cold water, the polymer retains its initial weight. In boiling water it hydrolyzes slowly. Investigation of pyrolytic stability, carried out by heating to 350° followed by evacuation, showed that the substance decreases in weight, but at a diminishing rate. Elemental analysis showed that the polymer differs from the initial dimethylphosphinoborine by a lower content

hydrogen, approximately three atoms per trimeric ring.

The second of the polymers formed upon irradiation is a glassy substance readily soluble in benzene; its molecular weight is 4700. Its elemental composition differs only slightly from that of the starting material. Upon prolonged heating in vacuum to 350°, the greater part of the polymer (67%) was converted into trimeric cyclic dimethylphosphinoborine, which was isolated as a sublimate.

The presence among the polymeric products of a fraction soluble in benzene and, in elemental composition, very close to the starting monomer made it possible to assume that, upon irradiation of trimeric cyclic dimethylphosphinoborine, ring cleavage occurs with the formation of a linear polymer whose molecule has an average length of 60–65 monomeric phosphinoborine units. This assumption is also confirmed by data on the effect of dose rate on the radiation yield of polymeric products (experiments 1 and 2, Table 1). Indeed, comparison of the results of these two experiments shows that the radiation yield of the polymer

Fig. 1. Thermomechanical curve of the polymer insoluble in benzene

Figure 1: Fig. 1. Thermomechanical curve of the polymer insoluble in benzene

soluble in benzene is inversely proportional to the square root of the dose rate, which indicates a chain radical mechanism for the formation of this polymer. At the same time, the yield of polymer insoluble in benzene does not depend in so simple a manner on the dose rate, and further studies are necessary to clarify the mechanism of its formation. On the other hand, the appreciable decrease in the hydrogen content in the benzene-insoluble polymer and the formation of gaseous products, as well as the strong change in the IR spectrum in the region 900-933 $cm^{-1}$, characteristic of the $CH_3$ group, and in the region 1000-1111 $cm^{-1}$, characteristic of the $BH_2$ group (see Fig. 2), indicates the possibility of the formation of radicals that can react with the starting molecules of trimeric phosphinoborine, eliminating hydrogen and combining into a polycyclic macromolecule.

**Fig. 1.** Thermomechanical curve of the polymer insoluble in benzene

Thus, two processes proceeding in parallel apparently occur according to the following scheme:

$$\text{trimeric cyclic dimethylphosphinoborine} \xrightarrow{\sim\sim\sim} \begin{array}{c} -BH_2-P(CH_3)_2-BH_2-P(CH_3)_2-BH_2-P(CH_3)_2- \\ \text{and} \\ \text{radical product of the ring} + H\cdot \end{array}$$

$$\text{radical product}+\text{trimeric cyclic dimethylphosphinoborine} \longrightarrow \text{polycyclic product}+H_2.$$

The possibility is not excluded of the initial formation only of a linear polymer which, under the experimental conditions, is capable of eliminating hydrogen with the formation of cross-links. However, such a scheme must be proved by special experiments on irradiation of the linear polymer.

## Experimental Part

The starting trimeric cyclic dimethylphosphinoborine $[(CH_3)_2PBH_2]_3$, m.p. 88-89° (lit. m.p. 86-87°), was obtained by the method described in ($^1$). All irradiation experiments were carried out in glass ampoules, which were evacuated for a long time before sealing. As an example, we give the description of experiment 3.

**Fig. 2.** IR spectra: *a* –starting trimeric cyclic dimethylphosphinoborine; *b* –polymer insoluble in benzene, obtained in experiment 3; *c* –polymer insoluble in benzene, obtained in experiment 4.

Fig. 2. IR spectra: a —starting trimeric cyclic dimethylphosphinoborine; b —polymer insoluble in benzene, obtained in experiment 3; c —polymer insoluble in benzene, obtained in experiment 4

Figure 2: Fig. 2. IR spectra: a —starting trimeric cyclic dimethylphosphinoborine; b —polymer insoluble in benzene, obtained in experiment 3; c —polymer insoluble in benzene, obtained in experiment 4

2.3 g of dimethylphosphinoborine was irradiated under the conditions given in Table 1. The resulting slightly yellowish substance was extracted with hot benzene. The benzene-insoluble precipitate weighed 0.93 g, yield 40%.

Found, %: C 33.48; H 9.62.
$C_6H_{21}B_3P_3$. Calculated, %: C 32.99; H 9.69.

The reduced viscosity of the solution in tricresol was 0.14. From the benzene solution, after removal of the solvent, a soft white substance was isolated. By evacuation at 250°/20 mm it was separated into sublimed starting dimethylphosphinoborine with m.p. 84-85° (0.70 g) and a glassy residue of 0.61 g (yield 27%).

Found, %: C 33.06; H 10.20.
$C_6H_{24}B_3P_3$. Calculated, %: C 32.51; H 10.29.

The reduced viscosity of the solution in tricresol was 0.07.

The polymer insoluble in benzene dissolves in cresol and hot dimethylformamide, and is sparingly soluble in tetrachloroethylene, carbon tetrachloride, and chloroform. After heating in a nitrogen atmosphere at 250° for 3 h and subsequent evacuation for 1 h, the polymer lost 12% in weight; the residue after the same procedure at 300° decreased in weight by another 5%, and at 350° by 3%. Altogether, after 9 h of heating within the range 250–350° and subsequent evacuation, the loss in weight amounted to 20%; at the same time the substance remained colorless. The solid residue after boiling in water for 2 h amounted to 68.7% of the initial weight and had a reduced viscosity of 0.09.

It has been established that, under the action of ionizing radiation on trimeric cyclic dimethylphosphinoborine, polymeric products of linear and polycyclic structure are formed.

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