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Abstract

Full Text

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STUDY OF THE RADIOLYSIS OF PIPERIDINE BY THE E.P.R. METHOD

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The study of the radiolysis and radiation oxidation of piperidine made it possible to conclude that the presence of the nitrogen heteroatom substantially changes the behavior of the cyclic compound as compared with a hydrocarbon of analogous structure ([1]). It was therefore of interest to determine, by the e.p.r. method, the nature of the primary products of the interaction of ionizing radiation with piperidine.

Piperidine (m.p. 269° K), purified as described in ([1]), was sealed under vacuum in ampoules made of special glass that gives no e.p.r. signal upon irradiation ([2]), and was exposed to γ-rays at 77° K and a dose rate of $5.2 \cdot 10^{16}$ eV/g · sec. The spectra, in the form of the first derivative of the absorption curve, were recorded on an RE-1301 radiospectrometer at 77° K. Solid vacuum samples of α,α'-diphenyl-β-picrylhydrazyl were used as the standard. The reactions of oxygen with irradiated piperidine were studied both on samples saturated before irradiation with molecular oxygen at room temperature and a pressure of 760 mm Hg, and after admitting O_2 to samples irradiated in vacuum.

Fig. 1. Dependence of the concentration of radicals on the irradiation dose of piperidine: 1 –in vacuum, 2 –in the presence of oxygen. Irradiation temperature 77° K.

In Fig. 1, curve 1 represents the dependence of the concentration of the radicals formed on dose during irradiation in vacuum. The linear character of the accumulation is preserved over the entire dose range from $5 \cdot 10^{19}$ to $1 \cdot 10^{21}$

eV/g, with a radiation yield $G = 5.5\dot{R}/100$ eV. In this same dose interval the structure of the e.p.r. spectra does not change. The signal is a poorly resolved doublet with a splitting of ~ 40 oersted (Fig. 2a).

On transition to higher temperatures in the range from 77 to 263° K, the concentration of radicals in the sample decreases by an amount determined in each case by the temperature jump. The character of the dependence of the radical concentration on time is shown in Fig. 3. After holding the samples at 193° K until a stationary state was reached, the temperature was raised at the moments designated by the points A, B, and C to 223, 256, and 258° K, respectively, and then at each temperature the kinetics of radical decay in vacuum was studied.

Comparison of the e.p.r. spectra in Figs. 2b and 2c shows that the doublet is preserved up to a temperature close to melting, and that with an increase in the holding temperature an additional splitting of the doublet into a triplet with $\Delta H \sim 7$ oersted appears. The observed changes in the signals indicate a decrease in the concentration of radicals and an improvement in the resolution of the spectra, but no transformations of some radicals into others were observed.

was detected. The primary character of the recorded radicals is confirmed by the fact that a spectrum consisting of a doublet of triplets was already detected at a dose of $9 \cdot 10^{17}$ eV/g in experiments in which the e.p.r. signals were recorded during irradiation at 93° K using a special X-ray installation ([3]). The spectrum presented for irradiated piperidine differs sharply from the spectrum of cyclohexane, which corresponds to the cyclohexyl radical ([4]). Since the piperidine spectrum lacks components that could be associated with cleavage of a C—H bond, the signal is evidently due to a radical whose unpaired electron is localized near the nitrogen atom. From the concepts developed by a number of authors in studying transformations of amines ([5,6,7]), it follows that under the action of ionizing radiation on frozen piperidine one may expect the formation of ion-radicals $C_5H_{10}NH^+$ according to

$$C_5H_{10}NH \rightsquigarrow C_5H_{10}NH^+ + e^-,$$

where the detached electrons are captured by traps in the solid phase. The doublet of triplets shown in Fig. 2 can be explained by using the interpretation given for the e.p.r. spectrum of irradiated ammonium perchlorate ([8]). In the latter case, the observed quartet of triplets is attributed to the ion NH_3^+, whose unpaired electron interacts with three protons and the nitrogen nucleus with different hyperfine-splitting constants. In irradiated piperidine an analogous role may be played by the ion-radical $C_5H_{10}NH^+$. The doublet structure of the spectrum with a splitting of ~ 40 oersted is explained here by the interaction of the unpaired electron with a proton, and the triplet structure by its interaction with the nitrogen nucleus.

Fig. 2. E.p.r. spectra of piperidine. *a*—irradiation in vacuum at 77° K, *b*—the same after holding at 193 and 223° K, *v*—the same after holding at 256° K, *g*—

Fig. 2. E.p.r. spectra of piperidine.

Figure 2: Fig. 2. E.p.r. spectra of piperidine.

Fig. 3

Figure 3: Fig. 3

irradiation in the presence of O_2 at 77° K and holding at 256° K. Temperature of recording the spectra: 77° K.

In work ([1]) it was shown that under the action of ionizing radiation on liquid piperidine in the absence of O_2, tetrahydropyridine and molecular hydrogen are formed in equimolar amounts. On the basis of the above interpretation of the e.p.r. spectra of irradiated frozen piperidine, the following assumption may be made regarding the mechanism of formation of these radiolysis products. As a result of neutralization of the ion-radical $C_5H_{10}NH^+$, arising in the primary act, by a thermalized electron released from a trap as the temperature is raised, an excited molecule $C_5H_{10}NH^{\#}$ is formed, which then decomposes according to the scheme:

$$C_5H_{10}NH^+ + e^- \rightarrow C_5H_{10}NH^{\#} \rightarrow C_5H_9N + H_2.$$

Such a reaction for the formation of tetrahydropyridine and H_2 is confirmed by the results of a study of the kinetics of radical decay, which show that, as the temperature is raised, the total concentration decreases without any change in the character of the signal.

When piperidine frozen in the presence of oxygen is irradiated, only a decrease in the concentration of radicals is likewise observed in comparison with vacuum samples. On accumulation curve 2 in Fig. 1, two regions with different slopes can be distinguished, the initial region being characterized by a yield $G = 2R/100$ eV. The difference in the kinetics of radical accumulation is not manifested in the character of their spectra, which are indistinguishable from the spectra of vacuum samples and remain unchanged over the same dose interval. Changes in the hyperfine structure of the spectra upon increasing the temperature and the kinetics of radical decay in vacuum and oxygen-containing samples (curves 4 and 6, Fig. 3) are also identical.

The identity of the spectra of the vacuum and oxygen-containing samples both at 77° K and after keeping them under identical conditions (Figs. 2b and 2c) makes it possible to conclude that, in the presence of O_2, peroxide radicals are not formed either during irradiation or upon subsequent raising of the temperature up to melting of the samples. Thus, radiation oxidation of piperidine with formation of the hydroperoxide $C_5H_{10}NOOH$, described in work ([1]), must proceed without the participation of peroxide radicals.

Fig. 3. Kinetics of radical decay in vacuum (1, 2, 3, 4, 5) and in the presence of oxygen (6) at temperatures: 1–163° K, 2–193° K, 3–223° K, 4–256° K, 5–258° K, and 6–256° K.

A possible interpretation of such a process, based on the mechanism of radiolysis in vacuum presented above, is the introduction of O_2 into the piperidine molecule according to the scheme

$$C_5H_{10}NH^+ + O_2^- \rightarrow [C_5H_{10}NH \cdot O_2]^{\#} \rightarrow$$

$$\rightarrow C_5H_{10}NOOH,$$

which assumes capture of a thermalized electron by an oxygen molecule. Such a mechanism explains the decrease in the radiation yield of radicals in the presence of oxygen. To confirm the proposed schemes, data are needed on the behavior of radicals and on the formation of final products under the same conditions.

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