STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF THE RADIOLYSIS PRODUCT OF CRYSTALLINE *o*-NITROANILINE

1965

SovietRxiv

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Abstract

Full Text

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STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF THE RADIOLYSIS PRODUCT OF CRYSTALLINE *o*-NITROANILINE

(Presented by Academician V. I. Spitsyn, February 13, 1965)

In the present work, the radiation-chemical transformation of crystalline *o*-nitroaniline under the influence of γ-radiation has been studied, and some chemical and physicochemical properties of one of the radiolysis products have been investigated.

Samples of *o*-nitroaniline in quartz test tubes were irradiated with free access of air by the γ-radiation of the IRT-2000 reactor of the Institute of Physics of the Academy of Sciences of the Georgian SSR, with a total dose of $10^2 n/\text{cm}^2 \cdot \text{sec}$ over 100 h. The total γ-radiation dose was 10^{23} eV.

Fig. 1. Bar diagram of the Debye pattern of the brown radiolysis product

Irradiation of crystalline *o*-nitroaniline is accompanied by a deepening of the color of the substance, and at total doses of 10^{23} eV the irradiated mass assumes a dark-brown color. On the basis of the insolubility of the obtained brown product in a number of organic solvents (CCl_4, benzene, ethyl alcohol, pyridine, tetrahydrofuran, boiling aniline, etc.), its isolation from the irradiated mass was carried out by successive washing of the solid substance with various organic solvents. In this process the unconverted *o*-nitroaniline, as well as other soluble radiolysis products, were washed out, while the brown product remained as a precipitate. The washing out with solvent was monitored by spectrophotometry of the solution.

The results of chemical microanalysis of the brown substance showed the following composition: H 3.53%, C 62.59%, N 17.91%, O_2 15.97% (obtained by difference).

The Debye pattern of the isolated brown product indicates its crystalline structure (Fig. 1). The substance does not melt when heated in an inert atmosphere up to 800°.

Fig. 2. IR absorption spectra

Figure 2: Fig. 2. IR absorption spectra

Investigation of the infrared absorption spectra of an emulsion of the brown substance in polyfluorinated hydrocarbon showed the presence of a broad absorption band in the region 3000–3500 cm^{-1}, with a center at about 3325 cm^{-1}, and with indistinct maxima at 3061, 3200, and 3155 cm^{-1}. It is known that in this region the bands of OH and NH stretching vibrations appear chiefly (1). The great width of the band observed by us makes it possible to assign it to vibrations of hydroxyl groups (Fig. 2).

Mass-spectrometric investigation* of the brown precipitate obtained from solid *o*-nitroaniline under the influence of radiation gave a maximum mass of the substance equal to 474 ± 2**. However, the specific properties of the brown product (insolubility in a large number of organic compounds, deep coloration, high thermal stability, compar-

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* Introduction of the substance into the mass spectrometer was carried out by evaporating it in high vacuum. A molybdenum strip with a recess for applying the substance served as the heater.

** The MI-1305 mass spectrometer used by us measures masses up to 500 units.

···fairly high electrical conductivity) make it possible to suppose that the molecular weight of this substance is much higher than the mass determined mass-spectrometrically. It may be thought that the indicated mass 474, as well as the smaller masses observed by us (341, 256, 150, 126), relate to decomposition products of the substance under consideration.

The specific electrical conductivity of the brown product at room temperature reaches 10^{-13} $\Omega^{-1} \cdot cm^{-1}$ and lies in the region characteristic of the electrical conductivity of organic semiconductors bordering on insulators ([2,3]). The electrical conductivity of most organic semiconductors lies in the range of values 10^{-10}–10^{-15} $\Omega^{-1} \cdot cm^{-1}$ at room temperature. With increasing temperature their electrical conductivity increases in accordance with the exponential law valid for intrinsic conduction.

Fig. 2. IR absorption spectra

From this point of view it was of interest to investigate the semiconductor properties of the product of the radiation-chemical transformation of *o*-nitroaniline.

The results of investigating the dependence of electrical conductivity on temperature for the brown product, given in Fig. 3, satisfy a linear dependence well. In the investigated temperature interval, dependences are obtained that are characteristic of impurity and intrinsic conduction. The activation energies, determined from the slope of the curve, are 0.29 and 0.8 eV, respectively. Such

Fig. 3. Temperature dependence of electrical conductivity

Figure 3: Fig. 3. Temperature dependence of electrical conductivity

a width of the forbidden band indicates that the semiconductor properties of the brown product are not connected with charring of the substance studied upon heating, since the forbidden band of graphite is narrower.

Fig. 3. Temperature dependence of electrical conductivity

The observed increase in the electrical conductivity of the brown product with temperature, and also the comparatively low value of its activation energy, make it possible to assume for this substance the existence of a large number of delocalized π-electrons. It may be supposed that, during the radiation-chemical transformation of *o*-nitroaniline, an enlargement of its molecules partly occurs and that the brown product under consideration contains a greater number of aromatic rings than the initial substance. Such a conception agrees well with the special properties of this substance (insolubility, deep color, high melting point). In addition, it is known that with an increase in the number of condensed aromatic rings and under the influence of heteroatoms, organic compounds acquire color ([2]), i.e., the magnitude of the quantum that transfers the molecule from the normal state to an energetically higher state decreases. At the same time, detachment of an electron from the molecule of a colored organic compound is facilitated, with the appearance in them of electrical conductivity.

Thus, the substance obtained in the radiolysis of solid *o*-nitroaniline should be regarded as an organic semiconductor.

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Received
11 II 1965

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