ADDITION OF MOLECULAR NITROGEN

CHEMISTRY

1965

SovietRxiv

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UDC 541.15

CHEMISTRY

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ADDITION OF MOLECULAR NITROGEN TO PERCHLOROCARBONS UNDER THE ACTION OF IONIZING RADIATION

(Presented by Academician S. S. Medvedev, 10 IV 1965)

The ability of molecular nitrogen to add to organic compounds under the action of ionizing radiation was first established in 1964. The radiation-chemical yield of nitrogen binding, $G(-N_2)$, depends on the nature of the hydrocarbon and did not exceed 1 molecule/100 eV.

To study the conditions for the addition of molecular nitrogen and to elucidate the nature of the products formed, the simplest perchlorocarbons—carbon tetrachloride and tetrachloroethylene—were selected. In this case the possibility of formation of nitrogen-hydrogen-containing groups and compounds was excluded. The relative simplicity of the radiolysis products, as well as the absence of radiation-initiated chain polymerization of tetrachloroethylene, facilitated interpretation of the results.

The starting compounds were subjected to thorough purification. Tetrachloroethylene was treated several times with dilute hydrochloric acid, washed with distilled water to a neutral reaction, dried over calcium chloride, and distilled on a rectification column. Chromatographic control showed the absence of impurities.

Irradiation was carried out in stainless-steel ampoules equipped with a manometer. γ-Radiation from Co^{60} was used; the dose rate was 280 rad/sec. The concentration of bound nitrogen in the radiolysis products was determined by the Kjeldahl method.

Upon irradiation of nitrogen solutions in tetrachloroethylene, the concentration of bound nitrogen is directly proportional to the absorbed dose in the range studied. The concentration of bound nitrogen increases with increasing pressure and temperature (Fig. 1). The dependence of the concentration of bound nitrogen has a more complex character in the case of irradiation of frozen solutions.

Fig. 1

Figure 1: Fig. 1

The concentration of bound nitrogen rapidly reaches a maximum value—in this portion of the curve $G(-\mathrm{N}_2) = 1.5$; with further increase in dose, the fixation yield decreases. Apparently, in this case fixation occurs only at the expense of nitrogen contained in the solid phase; its concentration decreases owing to the practical absence of diffusion from the gas phase.

In the pressure range studied, $G(-\mathrm{N}_2)$ increased linearly. The radiolysis products were analyzed by gas-liquid chromatography on a Perkin-Elmer model 451-D fractometer (Fig. 2). Comparison of chromatograms of products formed as a result of radiolysis in an atmosphere of nitrogen or argon revealed specific differences.

During radiolysis in an argon atmosphere, peak No. 2, located between the starting $\mathrm{C}_2\mathrm{Cl}_4$ (or CCl_4) and hexachloroethane, is completely absent from the chromatograms. The use of preparative gas-liquid chromatography will probably make it possible to isolate the nitrogen-containing compounds characterized by peaks No. 2 for their subsequent identification.

For investigation of the products of radiation fixation of nitrogen, spectral methods were used. The irradiated samples of tetrachloroethylene were dissolved in the initial C_2Cl_4 and analyzed with a recording spectrophotometer "Unicam."

Fig. 1. Dependence of the concentration of bound nitrogen on dose:
1 —in the presence of additives, 41°, 1.5 atm; 2 —41°, 1.5 atm; 3 —41°, 50 atm; 4 —167°, 50 atm and 41°, 120 atm; 5 —250°, 50 atm; 6 —320°, 50 atm; 7 —250°, 120 atm; 8 $-77^{\circ}K$, 120 atm

In the absorption spectra (Fig. 3) a characteristic band was observed with a maximum at 290-292 mμ. The optical density of the solutions at the absorption maximum increased linearly with increasing absorbed dose (Fig. 4). This band was completely absent in the UV absorption spectra of solutions prepared from tetrachloroethylene previously irradiated in an argon atmosphere.

From literature data it is known that, for groups $-N = N-$ located in cyclic systems, absorption in the region 250-320 mμ is characteristic, whereas the same groups in linear systems absorb in a longer-wavelength region.

Some information on the nature of the bonds and the possible structure of the nitrogen-binding products could be provided by IR spectra. For this purpose, IR spectra were recorded for tetrachloroethylene irradiated in atmospheres of nitrogen and argon. The spectra were taken on recording spectrophotometers UR-10 or IKS-14. In experiments carried out in a nitrogen atmosphere, an absorption band at 1656 cm^{-1} was observed; it was completely absent when radiolysis was carried out in an argon atmosphere.

Fig. 2

Figure 2: Fig. 2

Fig. 3. Absorption spectra of solutions of tetrachloroethylene radiolysis products irradiated in a nitrogen atmosphere

Figure 3: Fig. 3. Absorption spectra of solutions of tetrachloroethylene radiolysis products irradiated in a nitrogen atmosphere

Fig. 2. Left —chromatogram of irradiated tetrachloroethylene: thermal-conductivity detector, 2-meter column, 9% silicone elastomer E-301 with 1% polyfluoroalkylated resin on celite (80–100 mesh), temperature 180°, helium flow rate 55 ml/min. Asterisk —switching of the tape speed. Right —chromatogram of irradiated carbon tetrachloride (same conditions).

According to data of some authors, a band in the region of $\sim$ 1600 cm^{-1} is assigned to the diazo group, although, as a rule, these bands are weak and their identification is difficult. The products obtained in the radiolysis of tetrachloroethylene in a nitrogen atmosphere were reduced with metallic sodium in alcohol or with lithium aluminum hydride in tetrahydrofuran, followed by distillation and spectrophotometry in the IR region. In the region of 3500 cm^{-1} an absorption band appeared which was absent in the IR spectra of argon ···

samples subjected to similar operations. The appearance, after reduction, of a single band may indicate the formation of N—H groups, for which one band in the region 3500–3000 cm^{-1} is characteristic; for vibrations of the NH_2 group in this region two absorption bands are characteristic.

The mass spectra of the radiolysis products of perchlorocarbons are rather complex. Without going into detail, let us note that in the mass-number range studied, in the mass spectrum of the radiolysis products of tetrachloroethylene containing fixed nitrogen there is a series of peaks shifted by 28 units in comparison with the peaks observed in the mass spectrum of radiolysis products in an argon atmosphere.

Fig. 3. Absorption spectra of solutions of tetrachloroethylene radiolysis products irradiated in a nitrogen atmosphere

Fig. 4. Dependence of optical density at 290–292 mμ of solutions of tetra-

Fig. 4. Dependence of optical density at 290–292 mμ of solutions of tetrachloroethylene radiolysis products irradiated in a nitrogen atmosphere on the absorbed dose

Figure 4: Fig. 4. Dependence of optical density at 290–292 mμ of solutions of tetrachloroethylene radiolysis products irradiated in a nitrogen atmosphere on the absorbed dose

chloroethylene radiolysis products irradiated in a nitrogen atmosphere on the absorbed dose

From the temperature dependence of the rate of radiation fixation of nitrogen, the apparent activation energy of the process was estimated to be ~ 1.5 kcal.

The EPR spectrum of the radiolysis products of tetrachloroethylene irradiated in ampoules made of "Luch" glass in a nitrogen atmosphere with a dose of ~ 25 Mrad is characterized by a broad singlet with no signs of hyperfine structure. Illumination with a DKSSh-1000 lamp does not change the shape of the signal, but leads to a decrease in its intensity.

From the data presented, despite their preliminary character, some assumptions can be made about the possible nature of the nitrogen-fixation products. A number of facts, it seems to us, speak in favor of addition at the double bond:

1) the appearance of an absorption band corresponding to an NH bond, and not NH_2, after reduction of the nitrogen-containing products;
2) in the fixation of nitrogen by carbon tetrachloride, the value of $G(-N_2)$ is comparable with the value of the radiation-chemical yield of unsaturated products—hexachlorocyclobutene and hexachlorobutadiene—arising during the radiolysis of CCl_4;
3) the absorption band at 290–292 mμ lies in the region in which, according to the literature, absorption is characteristic of –N=N–groups in cyclic systems.

It is possible that cyclic structures of the diazine tetracycle type are formed:

$$\begin{array}{c} N=N \\ | \quad | \\ C-C \end{array}$$

It is very probable that, in the process of radiation fixation, a substantial role is played by the reaction of the molecular nitrogen ion with products of an unsaturated nature.

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Received
3 II 1965

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