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## Abstract

## Full Text

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# HYDRAZINOLYSIS—A NEW METHOD FOR STUDYING THE STRUCTURE OF NITROGEN-CONTAINING POLYMERS WITH CONJUGATED BONDS

*(Presented by Academician V. A. Kargin, 19 II 1964)*

The study of polyconjugated systems, as is known, is associated with serious methodological and experimental difficulties, primarily because the overwhelming majority of these compounds are insoluble and infusible substances. Therefore, the range of research methods has until now been practically limited only to the study of IR spectra, EPR spectra, and, in some cases, indirect judgments about the structure of polymers from the results of their thermal destruction. It should also be noted that, for polymers containing, along with C=C bonds, also C=N bonds, IR spectra do not make it possible to evaluate the ratio between these types of $\pi$-bonds. Therefore, one of the important tasks in the chemistry of polyconjugated systems is the creation of effective chemical methods for their investigation.

Among such methods may be included the destruction of polyconjugated systems with subsequent identification of low-molecular-weight products. Methods that make it possible to selectively cleave C=N bonds without affecting C=C bonds in aliphatic chains and aromatic rings acquire special significance.

As such a method we used the hydrazinolysis reaction of nitrogen-containing polymers with conjugated bonds.

The possibilities of this reaction were studied on a series of polymers belonging to the classes of polyazines and poly-Schiff bases, as well as on paracyanogen, products of thermal treatment of polyacrylonitrile, polymers obtained by polymerization with opening of heterocycles (pyridine and quinoline), etc.

The reaction was carried out by heating the polymer with an excess of hydrazine hydrate in an argon atmosphere at a temperature of 100°.

**Hydrazinolysis of polyazines.** As objects of study we took polyazines prepared on the basis of glyoxal, benzil, 4,4′-diacetyldiphenyl oxide, 4,4′-diacetyldiphenyl ether of ethylene glycol (1), and *p*-diacetylbenzene (2).

Hydrazinolysis of the polyazine from benzil ($M = 2200$) leads to deep destruction of the polymer. The final reaction product is the dihydrazone of the starting diketone—benzil. The melting point of this dihydrazone was 147-148° (lit. 147°) ($^3$).

| | | | |
|---|---|---|---|
| Found %: | C 70.70, 70.72; | H 5.81, 5.79; | N 23.57, 23.42 |
| $C_{14}H_{14}N_4$. Calculated %: | C 70.55; | H 5.82; | N 23.63 |

Hydrazinolysis of the polyazine from 4,4′-diacetyldiphenyl oxide leads to analogous results. The product of hydrazinolysis is the dihydrazone of the indicated diketone, which decomposes without melting when heated to 350°. The elemental composition of this substance is

| | | | |
|---|---|---|---|
| Found %: | C 68.52, 68.59; | H 6.28, 6.40; | N 20.47, 20.28 |
| $C_{16}H_{18}N_4O$. Calculated %: | C 68.06; | H 6.42; | N 19.84 |

Hydrazinolysis of the polyazine from glyoxal also proceeds practically completely, with formation of dark-colored water-soluble products.

Hydrazinolysis of polyazine from *p*-diacetylbenzene and 4,4′-diacetyldiphenyl ether of ethylene glycol proceeds somewhat differently. These polymers form products soluble in hydrazine only in part. After treatment with hydrazine, part of the polymer becomes infusible, which apparently is a consequence of the formation of crosslinked structures. The data of elemental analysis indicate that, as a result of the action of hydrazine on the indicated polyazines, the insoluble residue shows a decrease in carbon content and an increase in hydrogen and nitrogen content.

**Hydrazinolysis of poly-Schiff bases** was carried out under conditions analogous to those for polyazines. Poly-Schiff bases obtained by condensation of glyoxal ($^4$) and benzil ($^5$) with *p*-phenylenediamine were chosen as the objects of study.

The poly-Schiff base obtained from glyoxal and *p*-phenylenediamine, as a result of the action of hydrazine for 6 h, decomposes completely with the formation of dark-colored water-soluble products. If it is assumed that in this case as well the destruction proceeds at the $C = N$ bonds, the reaction products should be *p*-phenylenediamine and glyoxal dihydrazone.

Paper chromatography was used to identify these components.

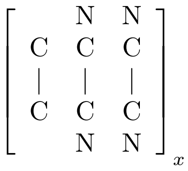
Methanol or a mixture of *n*-butyl alcohol—water—acetic acid (4:5:1) was used as the mobile phase. In the case of the ternary solvent mixture, a clear separation of the destruction products of the poly-Schiff base from glyoxal into two components was achieved. The distribution coefficients of these substances were found to be 0.94 and 0.70, respectively. The distribution coefficient of pure *p*-phenylenediamine under the same conditions is 0.69. The practical coincidence of the distribution coefficients of one of the components of the mixture of hydrazinolysis products and *p*-phenylenediamine, as well as the identical coloration obtained when the chromatograms were developed with a solution of ninhydrin in *n*-butyl alcohol, prove quite convincingly that this component is *p*-phenylenediamine.

This is also confirmed by the fact that, in chromatography using methyl alcohol as the mobile phase, the value of the distribution coefficient of the amine component ($R_f$ 0.56) likewise coincides with the distribution coefficient of *p*-phenylenediamine ($R_f$ 0.57). The destruction of the poly-Schiff base from benzil and *p*-phenylenediamine proceeds analogously.

In paper chromatography in methyl alcohol of the products of hydrazinolysis of this compound, *p*-phenylenediamine ($R_f$ 0.55) was also detected as one of the components. The second component, isolated in pure form by repeated recrystallization, had m.p. 147-148°. In determining the melting point of a mixture of this compound with benzil dihydrazone, specially synthesized for this purpose, a very slight depression of the melting point of the mixture occurred (by 1°) in comparison with the pure dihydrazone (m.p. 148°). Therefore it may be considered proven that, in the hydrazinolysis of the poly-Schiff base from benzil and hydrazine, the destruction products are benzil dihydrazone and *p*-phenylenediamine.

Thus, using polyazines and poly-Schiff bases as examples, it has been shown that, upon interaction with hydrazine, destruction of the polymers occurs at the C = N bonds, with the formation of dihydrazones and amines corresponding to fragments of the structure of the main polymer chain.

Paracyanogen, synthesized earlier in our laboratory, has the following structure (6,7):



$$\left[\begin{array}{ccc} & N & N \\ C & C & C \\ | & | & | \\ C & C & C \\ & N & N \end{array}\right]_x$$

This product is insoluble in ordinary organic solvents and dissolves only partially in concentrated sulfuric and formic acids.

During hydrazinolysis of paracyanogen under the above conditions, 16% of the starting compound underwent decomposition with the formation, as in the case of polyazine from glyoxal, of dark-colored, water-soluble compounds.

When hydrazine acts on polypyridine (8) and polyquinoline, destruction of the polymers also occurs.

The dark-colored products soluble in water and alcohols amount to 40% for polypyridine and 65% of the weight of the starting polymers for polyquinoline.

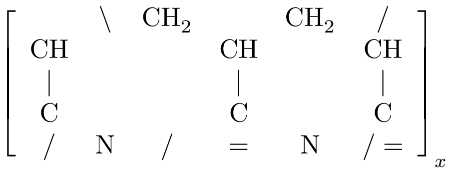
Paper chromatography of the destruction products of polyquinoline showed that this mixture consists of four components. The most readily eluted component, moving with the solvent front, gave a color reaction with ninhydrin, which indicates the amine character of this compound.

Adsorption chromatography of an aqueous solution of the destruction products of polyquinoline on an $Al_2O_3$ column led to an even clearer separation of the mixture into 4 components.

An amount of 34.8% of the initial weight of the product mixture was isolated as the most readily eluted amine component.

This indicates that the macromolecules of the indicated polymers consist of fragments separated by $C = N$ bonds. Consequently, the polymerization of pyridine and quinoline proceeds with opening of the heterocycle, which confirms the assumption advanced earlier.

The product of the thermal transformation of polyacrylonitrile, to which the following formula is ascribed ⁽⁹⁾, was also subjected to the action of hydrazine:



As a result of hydrazinolysis, no low-molecular-weight soluble reaction products were obtained. This was to be expected, if one takes into account that the formation of low-molecular-weight decomposition products requires cleavage of single or double carbon-carbon bonds, which do not undergo hydrazinolysis. Nevertheless, hydrazinolysis at $C = N$ bonds also occurs in this case, as evidenced by an increase in the weight of the polymer treated with hydrazine.

The course of hydrazinolysis is considerably facilitated if the polymer is at least partially soluble in the reaction medium. Thus, a poly-Schiff base obtained from *n*-phenylenediamine and benzil in the melt, and possessing very limited organic solubility, practically does not undergo hydrazinolysis when treated with hydrazine hydrate. However, if dimethylformamide, which is a good solvent for the indicated polymer, is added to the reaction mixture, hydrazinolysis proceeds almost completely.

In an analogous manner, it is possible to increase substantially the degree of hydrazinolysis also for polyazine from 4,4′-diacetyldiphenyl oxide (from 1–2 to 20%).

Thus, the study of the hydrazinolysis reaction of conjugated polymers containing C = N, using polyazines, poly-Schiff bases, polyquinoline and polypyridine, paracyanogen, and heat-treated polyacrylonitrile as examples, showed that hydrazine is a specific destructive agent for C = N-conjugated bonds.

The extent of hydrazinolysis depends in a definite way on the structure of the starting polymer.

On the basis of the data obtained, it may be assumed that the hydrazinolysis reaction of polymers containing conjugated C = N bonds in the main chain can serve as the basis for the detailed development of a new method for establishing the structures of polyconjugated systems containing C = N bonds.

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