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Abstract

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On the Reactions of Aromatic Diazo Compounds with Lignin

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Various lignins are high-molecular compounds based on phenylpropane residues containing groups of aliphatic alcohols, phenolic and enolic hydroxyls, as well as groups of simple ethers.

Industrial lignins, which are of great practical interest as a potential source of aromatic raw material for the chemical industry, differ from natural lignins in their physical and chemical properties; however, they also have many common chemical properties, determined by the fact that all lignins, both natural and isolated, have a common basis—the principal skeleton consisting of phenylpropane residues, and the differences in the bonds between these residues determine the differences in the properties of lignins.

Soluble industrial lignins (sulfite, sulfate, and sodium lignins) have a molecular weight of 7-10 thousand and a degree of polymerization of 40-45, whereas hydrolysis lignins have a three-dimensional structure and, as a result, are insoluble in any solvents; therefore their molecular weight cannot be determined.

Soluble industrial lignins contain, per phenylpropane residue (molecular weight 180), 0.3-0.5 free phenolic and enolic hydroxyls; therefore ordinary isolated lignins are polyhydric phenols, containing in each molecule from 12 to 25 phenolic, and partly also enolic, hydroxyls.

Considering the properties of lignins as substances of phenolic character, one could assume the possibility of their coupling with diazo compounds in an alkaline medium.

There are indications in the literature (^1) that, under the action of diazotized sulfanilic acid on beech wood, lignin dissolves and nitrogen-containing products are formed; however, the products obtained from the interaction of lignin with the diazo compound were not investigated.

Using numerous examples of the interaction of alkali, sulfate, natural, hydrolysis, and certain other lignins with diazo compounds, we have been able to show that a coupling reaction proceeds in an alkaline medium with the formation of colored azo derivatives. The direction of the reaction, its rate, and also the occurrence of side reactions depend on the nature of the diazo compounds used and on the process conditions (reaction temperature, pH of the medium, concentration of the reacting substances).

Proceeding from experimental data on the interaction of lignin with diazo compounds and taking into account current knowledge of the structure of lignin, it may be assumed that the reaction of formation of azo compounds can proceed in the ortho position to the phenolic hydroxyl group present in lignin, at position 5. In this case, about 0.3 azo group is formed per phenylpropane residue, which approximately corresponds to the formation of one azo group for each free phenolic hydroxyl.

The formation of azo compounds of lignin may be represented by the scheme:

$$\text{lignin fragment } + RN_2Cl \rightarrow \text{ lignin} - N = N - R \; + HCl.$$

The content of 0.3 azo group was checked by titration with $TiCl_3$, which is also confirmed by direct determination of nitrogen by Dumas' method.

The formation only of azo compounds in the interaction of lignin with diazo compounds takes place when the pH of the medium is not more than 10–10.5. At higher pH values, nitrogen is evolved and additional amounts of diazo compounds are bound to lignin, but no longer through azo groups; rather, by means of carbon–carbon bonds.

The number of attached residues of diazo-compound molecules was monitored by the accumulation of carboxyl groups in the case of reaction with diazocarboxylic acids, by the sulfur content in the case of interaction with diazotized sulfanilic acid, and by the increase in nitrogen content in the case of reaction with diazotized *n*-nitroaniline.

Thus, it has been established that in a strongly alkaline medium, for lignin the predominant reaction becomes that characteristic of the interaction of quinones with diazo compounds (2,3):

$$\text{quinone } + \mathrm{ClN_2}- \text{ cyclohexane-COOH } \rightarrow \text{ substituted quinone } + \mathrm{N_2} + \mathrm{HCl},$$

which in the case of lignin apparently proceeds according to the scheme:

$$\text{lignin fragment } + \mathrm{ClN_2}- \text{ cyclohexane-COOH } \rightarrow \text{ lignin derivative containing } -\mathrm{N{=}N}- \text{ and carboxyl-conta}$$

The question of the interaction of lignin with diazo compounds in the nitrogen-evolution reaction is currently being studied in more detail.

By the reaction of lignin with diazo compounds in an alkaline medium, numerous derivatives were obtained (4), among which lignins containing residues of anthranilic acid, aminonaphthoic acid, sulfanilic acid, *n*-nitroaniline, α-naphthylamine, aniline, and others were studied.

Under the action of diazotized benzidine, *n*-phenylenediamine, and certain other disubstituted aromatic amines on lignins dissolved in alkali, their interaction proceeds with the formation of cross-linked po-

polymers characterized by insolubility in acids, alkalis, and organic solvents.

Reaction of lignin with diazotized sulfanilic acid (the preparation of azobenzenesulfonic acid derivatives of lignin was carried out jointly with graduate student Ha Chu-chi).

Sulfate lignin, precipitated from black liquor of the Svetogorsk Pulp and Paper Combine with carbon dioxide at a temperature of 70° and a carbon dioxide pressure of 4 atm, was deashed by heating with dilute hydrochloric acid and had the following composition: C 62.3, H 5.83, S 1.48, OCH_3 12.6, OH (by the acetylation method) 10.24%, phenolic hydroxyls by reaction with $Ba(OH)_2$: 0.6 groups per phenylpropane unit.

To a solution of sulfate lignin in alkali, a cooled solution of diazotized sulfanilic acid was added. As a result of the reaction, water-soluble products are obtained, containing sulfur in the form of sulfo groups and nitrogen in the form of azo groups.

Since the derivatives of lignin and sulfanilic acid are readily soluble in water and are not precipitated from solution by the action of acids, a special method for isolating the products was used. It consisted in precipitating the compounds obtained with cobalt chloride, filtering and washing the precipitate obtained, decomposing this product with alkali, filtering off the $Co(NH_3)_4Cl$ that separated, and passing the filtrate through cation-exchange resins. As a result, pure ligninazo-benzenesulfonic acid was obtained, which was then evaporated in vacuo, dried, and examined.

The analysis of the products obtained is given in Table 1.

Table 1

Ratio of lignin to diazosulfanilic acid	Yield of product from lignin taken, %	Sulfur content, %	Nitrogen content, %
1 : 1.0	152	4.0	3.46
1 : 1.5	198	8.2	3.0
1 : 2.0	241	10.0	–
1 : 2.5	271	10.0	2.78
1 : 3.0	281	10.2	–

As is evident from the data presented, the nitrogen content in all cases corresponds to approximately 0.3 azo-group residue per phenylpropane elementary unit of lignin. In addition, a reaction of the type of coupling with quinones also takes place, as indicated by the considerable accumulation of sulfur in the product obtained, with the increase in the number of sulfo groups ending mainly after 2 molecules of diazo compound have reacted for every 180 g of lignin.

Table 2

Ratio of lignin to diazoanthranilic acid	Yield relative to theoretical, %	Content, %	Content, %
		nitrogen	COOH
1 : 1	70	2.7	11.73
1 : 2	68	2.67	15.88
1 : 3	75	3.10	20.25

Reaction of lignin with diazotized anthranilic acid (the preparation of anthranilic acid derivatives was carried out jointly with graduate student T. M. Kroshilova).

For the study the same lignin was taken as in the preceding case; in alkaline solution it was treated with diazotized anthranilic acid. As a result of the reaction, products were obtained that are soluble in alkalis and precipitated from solution under the action of mineral acids.

Table 2 gives the results of the work.

The nitrogen content was determined by the Dumas micromethod. Determination of the azo group by titration with $TiCl_3$ according to the usual procedure gave approximately the same (5–10% lower) amounts of nitrogen.

Thus, in the interaction of diazoanthranilic acid with lignin in an alkaline medium, two processes take place: coupling with lignin (as with phenol) and a reaction with evolution of nitrogen, as a result of which carboxyl groups accumulate in addition to those that are attached to lignin as a result of azo coupling.

Reaction of lignin with other diazo compounds

Coupling of lignin with diazotized *p*-nitroaniline was carried out. As a result of the reactions, a product was obtained containing, at a lignin to diazo-*p*-nitrobenzene ratio of 1 : 1, 11.5% nitrogen, and, when the products were allowed to interact in a ratio of 1 : 2, 13% nitrogen. As in the preceding cases, two processes occur in an alkaline medium—one with the formation of azo compounds and the other with evolution of nitrogen and the production of arylated lignins containing nitro groups.

Coupling of lignin with diazotized α-naphthylamine made it possible to obtain a product containing, for each phenylpropane residue of lignin, up to 1.5 naphthyl radicals. Of these, 0.3 naphthyl radical per phenylpropane group is attached through an azo group, while the rest are attached with evolution of nitrogen. The product containing naphthyl radicals is soluble in benzine and benzene, whereas the original lignin is completely insoluble in hydrocarbons.

Products of the interaction of lignin were also obtained with diazotized: metanilic acid, β-naphthylamine, aniline, aminophthalic acid, benzidine, *p*-phenylenediamine, and others.

Study of the infrared spectra of the products obtained and comparison of them with the spectrum of the initial sulfate lignin in all cases gave new absorption bands characteristic of azo compounds (750 cm^{-1}). In the reaction with diazotized anthranilic acid, along with the new bands of the azo compound, distinct bands of carboxyl groups appeared (1710 cm^{-1}). In the reaction with diazotized *p*-nitroaniline, new bands at 1310 and 1550 cm^{-1} appeared, characteristic of the stretching vibrations of nitro groups.

It has been established that isolated lignins can react with diazo compounds in an alkaline medium. The reaction, depending on the pH of the medium, can proceed in two directions. First, coupling of diazo compounds with lignin occurs as with phenol, and an amount of azo groups can be obtained equal to the number of free phenolic hydroxyls in which position 5 in the ortho position to the phenolic hydroxyl is not occupied. Second, in a strongly alkaline medium, addition products are formed through a carbon–carbon bond with evolution of nitrogen. The method of interaction of lignins with diazo compounds makes it possible to obtain modified lignins containing functional groups new to lignin, which make it possible to change the physical and chemical properties of this polymeric material.

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