OXIDATION OF LIGNIN IN AQUEOUS ALKALINE SOLUTION

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The action of alkali on lignin and the chemistry of the processes taking place under these conditions are treated differently by different authors [1-12]. Many assume that the processes may take place by an ionic mechanism. In some papers [10-12] the process of alkaline delignification is considered as complex, taking place with the participation of free radicals which have been detected by the EPR method. The addition of sulfur and of ionol (2,6-di-tert-butyl-p-cresol) decreases the magnitude of the EPR signal in the products [12]. The EPR signal in lignins isolated by means of alkali is considerably higher than that in lignins obtained by mild methods [13]. This shows that under the action of alkalis on lignin homolytic processes take place as well as heterolytic ones.

In our opinion the decisive role in the appearance of homolytic processes is played by quinoid structures, whose presence in natural lignin has been shown by Freudenberg [14], in biochemical lignins by Chudakov [15], and in technical lignins by a number of authors [16]. Quinones, being electron acceptors, are capable of removing electrons from hydroxyl ions and converting them into hydroxyl radicals. The high reactivity of hydroxyl radicals interferes with recording them by physical methods. Blyumenfel'd et al. [17] have shown their presence by an indirect method. Consequently, in alkaline solution the reaction $OH^- + A \rightarrow OH + A^-$, leading to homolytic processes, may take place. Since the hydroxyl radical is a powerful oxidizing agent, its presence must lead to the appearance of oxidative processes in the system. In order to find out whether similar processes take place in the action of alkalis on lignin, we performed the hydrolysis and hydrogenolysis of hydrolyzed technical lignin from cotton husks and its models in an aqueous alkaline medium and studied the reaction products. The yield and composition of the soluble products change with variations in the conditions of the process, the maximum amount of soluble products being obtained by hydrogenolysis (Table 1). The composition of the phenolic fractions from these experiments was

TABLE 1. Yield and Composition of the Soluble Products under Various Degradation Conditions

No.	Components of the mixture	Charge, g	Process cond., T, °C; τ, h	Yield of solubles, %			Group comp. of the ether solubles, %		
				total	acetone soluble	ether soluble	phenol	acids	neutral substances
1	Cotton lignin NaOH	100 30	350; 1	30,4	6,70	23,70	9,12	4,56	10,02
2	Cotton lignin NaOH Phenol Water	100 30 20 300	350; 2	42,4	2,70	38,18	13,38	9,30	15,50
3	Cotton lignin NaOH Phenol CoS Water	100 15 20 2,0 300	360; 2	69,5	12,50	57,00	28,61	11,17	17,22

Note. In cases where phenol was added the added phenol is deducted from the yield. In experiment 3 the initial hydrogen pressure was 100 atm.

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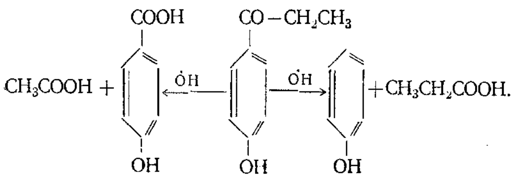
TABLE 2. GLC of Phenol Fractions from Cotton Husk Lignin Obtained under the Conditions of Table 1 (Apiezon L, t 200°C)

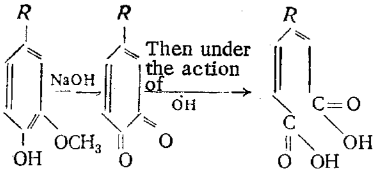
Substance determined	Relative retention time	Mixture in Exp., %		
		1	2	3
Phenol	1,0	6,1	27,0	38
o-Cresol	1,3	11,6	15,4	13,8
m- and p-Cresols	1,43	—	21,0	11,9
Not identified	1,77	—	—	5,2
o-Ethylphenol	1,80	12,4	8,0	12,5
2,5-Xylenol 3,5-Xylenol p-Ethylphenol	2,15	—	16,0	11,2
Not identified	2,30	19,1	—	3,2
Not identified	2,52	23,2	—	—
3,4-Xylenol	2,70	—	6,4	2,9
Pyrocatechol	3,20	—	3,4	—
Not identified	3,52	—	—	—
Hydroquinone	3,60	15,9	2,0	—
n-Propylguaiacol	4,10	—	0,8	—
Not identified	4,44	9,4	—	1,3
Not identified	5,86	2,3	—	—

studied. When aqueous alkali acted on cotton husk lignin, the chromatographable part of the phenolic fraction (Table 2, Expt. 1) contained 15.9% hydroquinone. If the action of alkali is combined with the action of phenol (Expt. 2), the amount of hydroquinone falls to 2%, but catechol appears simultaneously in the mixture. On hydrogenolysis (combined action of alkali, phenol, and hydrogen) no dihydric phenols appear in the phenolic fraction. We have found hydroquinone previously [18] in the neutral product from the hydrogenolysis of technical spruce and cotton lignins. The presence of hydroquinone in the phenolic hydrolysis fraction and the neutral hydrogenolysis products confirms the hydroxylation of the aromatic nucleus, since hydroquinone is not present in the structural fragments of lignin and can arise only as a result of a hydroxylation reaction.

The characteristics and behavior of the model substances in the hydrogenolysis process is also informative; under the action of alkali in a reducing medium acids are formed in addition to phenols. The yield of phenols in the hydrogenolysis of 1-(4-hydroxyphenyl)propan-1-one is 83.7% and the yield of acids is 16.3%, while in 1-(4-hydroxy-3-methoxyphenyl)propan-1-one the yields of phenols, acids, and neutral substances are 5.5, 49, and 45.5%, respectively, i.e., acids are formed in both cases. The phenolic fraction from 1-(4-hydroxyphenyl)propan-1-one was found (by the GLC method) to contain 64% phenol, 7% o-cresol, 8.5% m- and p-cresols, 3.5% p-ethylphenol, 11% p-propylphenol, and 6% of an unidentified compound. Eighty-five percent of the acids were distilled off (the remaining 15% being accounted for by the residue in the flask and losses). The distillation products contained 99.5% propionic acid, with acetic acid as an impurity, and 0.5% of a mixture of p- and o-hydroxybenzoic acids. The nature of the products formed once again confirms the existence of oxidative processes in the presence of aqueous alkali even in a reducing medium (hydrogenolysis). This process consists of hydroxylation of the α- and β-carbon atoms of the propane chain with subsequent cleavage of the bond between the nucleus and the aliphatic chain or between the α- and β-carbon atoms of the chain. For example, in the hydrogenolysis of the 1-(4-hydroxyphenyl)-propan-1-one model we showed the formation of products whose presence can be explained by hydroxylation reactions.



The low yield of phenols (5.5%) and the high yield of acids (49%) in the hydrogenolysis of 1-(4-hydroxy-3-methoxyphenyl)propan-1-one in a reductive medium, in comparison with the yield from 1-(4-hydroxyphenyl)propan-1-one, shows that more extensive oxidative processes take place in this case due to the possible formation of o-quinoid structures. Aliphatic acids (formic, acetic, and propionic) comprise 40% of the acids. Aromatic hydroxy acids are decarboxylated to phenols during distillation. Part of the acids is found in the form of humic acids. In the (4-hydroxy-3-methoxyphenyl)propan-1-one model the losses and still residue amounted to 19.3% of the total acids. The guaiacylpropane units can react with the cleavage of the aromatic nucleus in the following manner:



In this case, the direct hydroxylation of the aromatic nucleus takes place.

We did not find either muconic or maleic acid in the oxidation product. The presence of butyric and caproic acids in the acid products of the hydrogenolysis of lignin shows that the main route for their appearance is the cleavage of the aromatic ring [19].

To confirm the possibility of decarboxylation of the hydroxyaromatic acids, we carried out the hydrogenolysis of p-hydroxybenzoic acid (Table 1, conditions of Expt. 3). The total yield of ether-soluble products amounted to 70%, comprising 85.7% phenols and 14.3% acids (no neutral products were found in this case). The main phenolic product was phenol itself (99%), with only 1% of o- and p-cresols. The composition of the acids was not studied. This experiment confirms the possibility of phenols forming through the decarboxylation of hydroxy acids under the hydrogenolysis conditions.

Consequently, the hydrolysis and hydrogenolysis of lignin and its model substances in an aqueous alkaline medium are complex processes. The first stage consists of ionic reactions but, when quinone and quinone methide structures are present the hydroxyl ions react with the latter, forming hydroxyl radicals and giving rise to oxidative processes which take place even during hydrogenolysis in the presence of hydrogen and a catalyst.

EXPERIMENTAL

The material subjected to study was cotton lignin isolated by the hydrolysis of cotton husks with H_2SO_4 and having the following characteristics: difficultly hydrolyzable substances, 13% (there were no reducing substances), methoxy groups, 2.75%; hydroxy groups by Verley's method, 5.9%; moisture content 5%; ash content 5.5%; acidity to methyl orange calculated as acetic, 1.05%; bulk density, 0.43 g/cm^3.

The model compounds, 1-(4-hydroxyphenyl)propan-1-one and 1-(4-hydroxy-3-methoxyphenyl)propan-1-one, were obtained by methods described in the literature [20].

The hydrogenolysis of the model substances and the lignins and the hydrolysis of the lignins were carried out in a type NF-1 (Hungary) 1-liter rotating autoclave with electric heating. The calculated amount of the model substance or the lignin was mixed with a 5% solution of caustic soda (1 : 3), then catalyst CoS (2% on the substance) was added and then, if using an inhibitor, the inhibitor. The mixture was transferred quantitatively into the autoclave. On hydrogenolysis, an initial hydrogen pressure of 100 atm was established from a cylinder.

At the end of the process the contents of the autoclave were transferred to a beaker, and the autoclave was rinsed twice with water.

Separation of the Ether-Soluble Products. The alkaline hydrogenolyzate or hydrolyzate was acidified to pH 1 and extracted with ether. The ethereal solution was filtered to eliminate resins and insoluble products and was dried with anhydrous Na_2SO_4. Then the Na_2SO_4 was removed by filtration, the ether was distilled off, and the sum of the ether-soluble substances was determined. When separated into fractions, the ethereal extract was washed repeatedly and successively with a 10% sodium carbonate (Na_2CO_3) solution to extract the acids and with a 10% caustic soda solution to extract the phenols. The neutral substances remained in the ethereal solution. The sodium carbonate and caustic soda solutions were acidified and quantitatively extracted with ether. After drying, filtration, and evaporation of the ether, the acid and phenol fractions were obtained.

Analysis of the Phenol Fractions. Analysis was carried out by the GLC method on a Tswett 1-64 chromatograph. Polyesters (of diethylene glycol and adipic acid and of ethylene glycol and succinic acid), polyethyleneglycol-6000, and Apiezon L, 20% on INZ-600, support were used as the stationary phases; the rate of flow of the carrier gas, hydrogen, was 60 ml/min; the bridge current was 200 mA; the sensitivity was 1; the length of the column was 1 m; and the diameter was 4 mm (see Table 2).

CONCLUSIONS

The hydrogenolysis and hydrolysis of lignin in an aqueous alkaline medium must be considered as an oxidative degradation of the lignin macromolecule by hydroxyl radicals. This process takes place even in a reducing medium in the presence of a catalyst. This was shown by a study of the hydrogenolysis process using model compounds. The oxidative processes in lignin are connected with the appearance in the system (lignin or its model) of alkali-induced quinoid structures which, being electron-acceptors, abstract electrons from hydroxyl ions and form hydroxyl radicals. The latter lead to oxidative processes through the

the hydroxylation of the system. The correctness of this has been confirmed by studying the composition of the products, which shows the oxidative nature of the hydrogenolysis process.

LITERATURE CITED

1. N. I. Nikitin, Wood Chemistry [in Russian], Moscow–Leningrad (1951), p. 247.
2. H. Adkins and R. Frank, J. Am. Chem. Soc., 63, 549 (1940).
3. Z. A. Rogovin and N. N. Shorygina, The Chemistry of Cellulose and Its Accompanying Substances [in Russian], Moscow (1953), p. 607.
4. V. M. Nikitin and A. V. Obolenskaya, Bum. prom., No. 12, 1 (1953).
5. V. M. Nikitin, Lignin [in Russian], Leningrad (1961), p. 148.
6. M. Ya. Zarubin and V. D. Tishchenko, ZhPKh, 32, No. 2, 395 (1959).
7. M. Ya. Zarubin and V. D. Tishchenko, ZhPKh, 33, No. 11, 2576 (1961).
8. J. Gierer and Lief Åke Smedman, Acta Chem. Scand., 19, No. 5, 1103 (1965).
9. J. Gierer and N. H. Wallin, Acta Chem. Scand., 19, No. 6, 1502 (1965).
10. T. N. Kleinert, Tappi, 49, No. 3 (1966).
11. T. N. Kleinert, Tappi, 48, No. 2, 53 (1965).
12. T. N. Kleinert and J. Morton, Nature, 196, 334 (1962).
13. M. I. Chudakov, V. E. Bronovitskii, V. M. Mal'tsev, and M. G. Okun, in: Tr. VNIIGSa, 15, 276, Moscow (1966).
14. K. Freudenberg, Sci. 148, No.3670, 595 (1965).
15. M. I. Chudakov and A. P. Samsonova, in: Tr. VIIGSa, 15, 258, Moscow (1968).
16. B. D. Bogomolov, S. B. Pal'mova, and E. D. Gel'fend, in: Wood Chemistry, Vol. 1, No. 2 Riga (1968), pp. 93-94.
17. S. I. Sholina, G. F. Fomin, and L. A. Blyumenfel'd, ZhFKh, 43, No. 3, 800 (1969).
18. V. E. Bronovitskii, L. L. Kalinskaya, and D. R. Ikramova, Uzb. Khim. Zh., No. 1, 67 (1968).
19. V. E. Bronovitskii, M. A. Volochkovich, L. L. Kalinskaya, and Sh. Nam, Uzb. Khim. Zh., No. 3, 69 (1968).
20. R. G. Adams, (editor), Organic Reactions [Russian translation], Moscow (1948), No. 1, p. 455.