Russian Chemical Reviews **68** (11) 937 – 956 (1999) © 1999 Russian Academy of Sciences and Turpion Ltd

UDC 547.992.3 : 634.0.813

Reactivity of lignin and problems of its oxidative destruction with peroxy reagents

V A Demin, V V Shereshovets, J B Monakov

Contents

I.	Introduction	937
II.	Lignin structure	938
III.	Oxidation of model compounds	940
IV.	Combined action of oxidants on the sulfate pulp lignin	949
V.	Lignin activation towards oxidative action of oxygen and hydrogen peroxide	950
VI.	Ozonolysis of sulfate pulps	951
VII.	A schematic approach to the selective destruction of residual lignin with peroxy reagents	952
VIII.	Kinetic methods for assessment of residual lignin reactivity	953
IX.	Conclusion	954

Abstract. Published data on reactivity and oxidation of lignin and model compounds with hydrogen peroxide, ozone and chlorine dioxide as well as on oxidative destruction of the sulfate pulp lignin with various reagents during bleaching are systematised and generalised. Concepts of lignin activation towards its selective oxidation and kinetic features of sulfate pulp oxidative delignification are considered. The bibliography includes 157 references.

I. Introduction

Wood represents a complex polymeric composition in which lignin and cellulose are the main components.[1–7] During its processing, lignin and cellulose undergo a variety of parallel redox transformations and behave as a single complex (technical pulp).

Selective oxidative destruction of lignin in pulp, especially in sulfate pulp where lignin has been modified during the sulfate pulping process of the native polymer, is a difficult problem, mostly due to the complexity of lignin, which is built up of a multitude of non-uniform structural elements, and the extremely high variability of properties of this polyfunctional polymer.

The problem of oxidative destruction of residual lignin † with peroxy reagents [O_3, RC(O)OOH, H_2O_2] is of considerable practical importance since current manufacture of pulps (predominantly of sulfate pulps) consumes a million tons of chlorine for bleaching and results in toxic chlorine-containing pollutants, including dioxins.

The known multi-step schemes for complete oxidative destruction of the residual lignin with various sets of reagents have been developed empirically. Such schemes usually have no solid physicochemical background and, as a result, do not always take into account the impact of the preceding technological operations on the physicochemical properties of the residual lignin and the effect of acid-base catalysis. Consideration of these factors takes on especial significance on replacement of the chlorine and chlorine-containing compounds (used so far in the pulp industry) by hydrogen peroxide, oxygen and ozone, which are ecologically friendly but possess relatively low reactivities towards lignin.

The reactivities of the native and residual lignins in pulps and the mechanisms of lignin reactions with various reagents during pulp preparation from a wood raw material have been considered in a series of reviews.[4,8–10] The last two of them,[9,10] present a survey of the mechanisms of elementary reactions and characteristics of the majority of reagents used in wood chemistry and depict reaction schemes for the low-molecular-weight compounds that model lignin fragments. However, all these data allowed one only to explain rather than to predict the results of the action of any particular oxidant on the residual lignin. This is associated with the fact that the oxidative destruction of the residual lignin during pulp delignification is usually performed in several stages, because lignin cannot be selectively and completely oxidised in one step with any particular reagent.

It should be noted that lignin (more correctly, lignins) represent chemically labile polyfunctional polymers, which cannot be isolated as individual compounds in native states. Consecutive stages of oxidative destruction on each occasion deal with a 'different' lignin of a lignino-cellulose composition (technical pulp). Any chemical action on lignin not only alters its functional and polymeric composition but it also changes the number, ratio and strength of electrophilic and nucleophilic centres and the contents of 'weak' bonds in a lignin macromolecule.

The necessity to account for, and systematise, all the above-mentioned factors has led to the development of a new approach, in which the multi-step process of oxidative destruction of the residual lignin is considered as a united combination of redox transformations, wherein each particular stage 'prepares' and activates lignin for the subsequent technological stage through creation in lignin of new centres reactive towards nucleophilic or electrophilic reagents.

† Lignin that remained in the sulfate pulp after cooking.

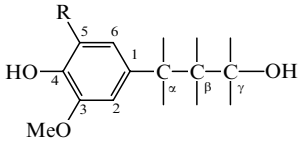
V A Demin Institute of Chemistry, Komi Scientific Centre of the Russian Academy of Sciences, Pervomaiskaya ul., 167000 Syktyvkar, Russian Federation. Fax (7-821) 243 66 77. Tel. (7-821) 243 24 27.
E-mail: kav@chemi.komi.ru
V V Shereshovets, J B Monakov Institute of Organic Chemistry of the Ufa Scientific Centre of the Russian Academy of Sciences, prosp. Oktyabrya 71, 450054 Ufa, Russian Federation. Fax (7-347) 235 60 66.
Tel. (7-347) 235 61 66 (J B Monakov).
E-mail: chemorg@academy.bashnet.ru

Received 26 October 1998
Uspekhi Khimii **68** (11) 1029 – 1050 (1999); translated by S V Chapyshev

This review includes a brief description of the lignin structure, a consideration of the reactions of some model compounds which are hard to oxidise with oxygen, hydroperoxide anions, ozone and chlorine dioxide as well as delignification of the sulfate pulp with hydrogen peroxide and ozone and activation of lignin towards its oxidative destruction with various reagents. It also introduces a concept of selective lignin oxidation by consecutive action of peroxy reagents, which has led to the development of the most efficient schemes for pulp bleaching. In addition, the kinetic features of oxidative lignin destruction in the processes of the sulfate pulp delignification are discussed.

II. Lignin structure

Lignins represent macromolecular polyfunctional aromatic compounds; a structural model of softwood lignin according to Freudenberg is described in Scheme 1. Being the components of wood tissues, lignins are responsible for vital mechanical, chemical and biological functions,[1–4] *viz*., they impart durability and protection against oxidation and microbial action. Lignin is biosynthesised in close proximity to macromolecules of cellulose and non-cellulosic polysaccharides, which results in a lignin–carbohydrate polymeric matrix. Chemical, physicochemical and mechanical interactions of lignin with cellulose ensure the formation of a complex polymeric composition, *viz*., the wood tissue, and predetermine the reactivities of its main components in chemicotechnological processes. Wood lignins are built up of substituted phenol–propane units. Guaiacyl- and syringylpropanol units are the most common structural elements.[11–17]



R = H, OMe.

The structural units are linked to each other with various ether and carbon–carbon bonds.[18–21]

Because of structural irregularity and great variety of the chemical bonds in lignin, the description of its macromolecule as a simple combination of a few (or a multitude of) monomers (substituted phenol–propane units) seems to be impossible.[22–26] The structure of lignin is still the subject of model studies.[27–30]

Several lignin structures, *e.g*., that shown in Scheme 1,[28] have been proposed based on the results of studies of lignin ethanolysis, thioacetolysis, oxidation[31–33] and hydrogenolysis[34] products, data of elemental analysis, functional group determinations, comparative analysis of properties of native lignin and synthetic dehydropolymers (DHP) built of substituted phenol–propane units, spectroscopic data (^{1}H and ^{13}C NMR, IR, UV),[20,22,35,36] the results of gel and gas chromatography and mass spectrometry. A segment of lignin macromolecule represented in the Freudenberg scheme contains 18 phenol–propane units and reflects the ratio of the main types of structural units, bonds and functional groups. This scheme can be supplemented by alternative structural elements, *e.g*., 6b, 13b, 14b, 13c and 14c. Later, Adler[37] suggested a structural scheme for a segment of the fir-wood lignin

Scheme 1

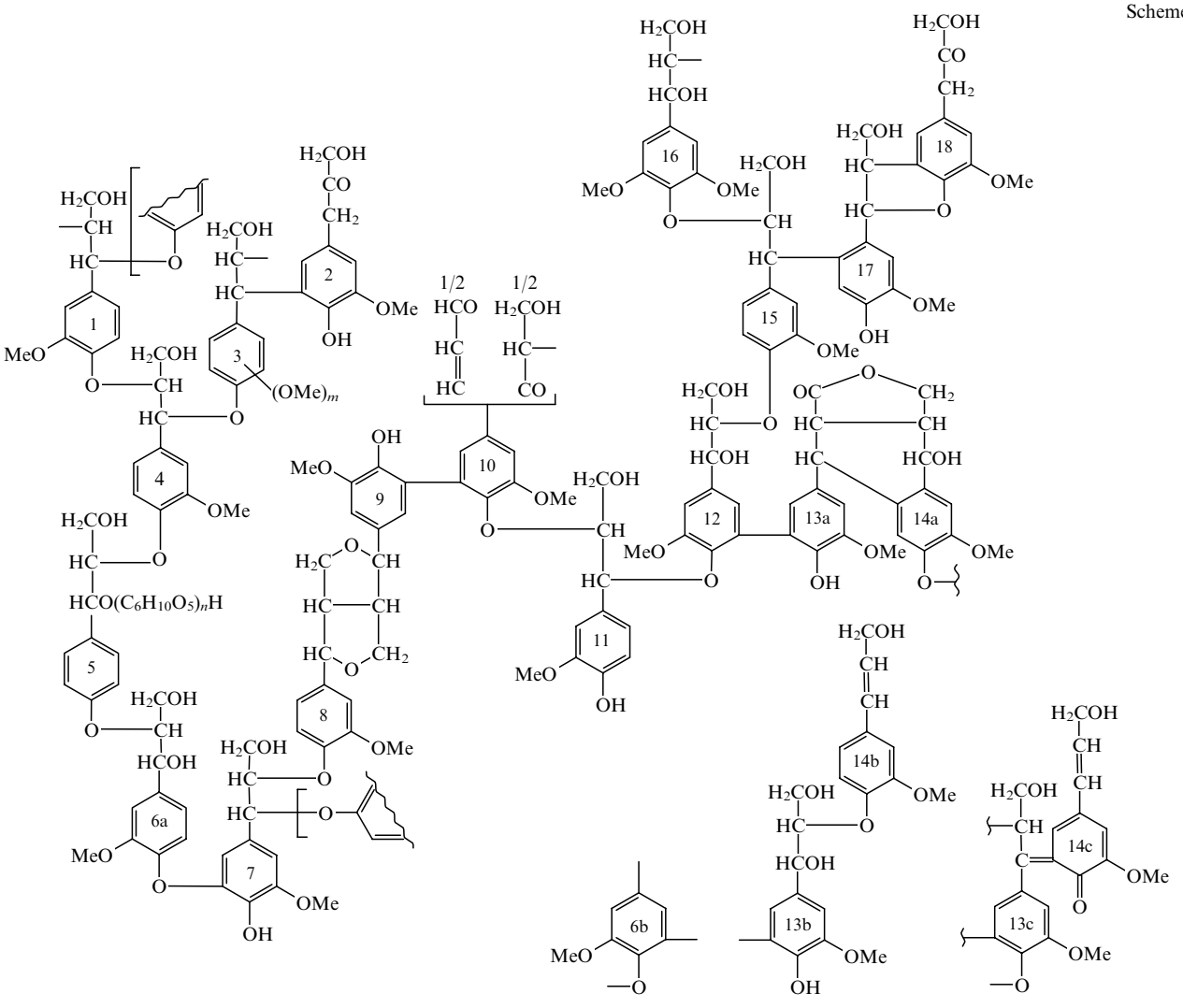


Table 1. Types and number of linkages between the structural elements in different lignin models.[18]

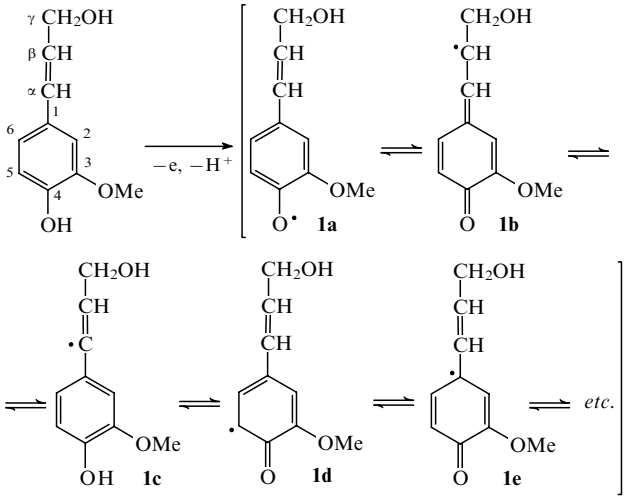
Linkage type	Number of linkages per 100 phenol–propane units [a]		
	I	II	III
C(β)–O–C(4)	55	65	49–51
C(α)–O–C(4)	–	–	6–8
C(β)–O–C(5)	16	6	9–15
C(β)–C(1)	9	15	2
C(5)–C(5)	9	2.3	9.5
C(4)–O–C(5)	3	1.5	3.5
C(β)–C(β)	2	5.5	2
C(α)–O–C(γ)	10	–	–
C(α)–C(β)	11	2.5	–
C(β)–C(6), C(6)–C(5)	2	–	4.5–5.0 [b]

[a] I, the Glasser model,[39] II, the Nimz model,[41] III, the Erickson model.[40]
[b] Including the C(1)–O–C(4) and C(1)–C(5) bonds.

macromolecule comprising 16 phenol–propane units. It is obvious that in such small segments it is rather difficult to take precisely into consideration the ratio of certain lignin structural elements and bonds. A recently proposed [38] model of fir-wood lignin contained 28 phenol–propane units and included some alternative structural elements that were previously absent in the Adler scheme. In addition to the models with a relatively small number of phenol–propane units built up by random combination of functional groups, bonds and structural elements, several more complete computer structural models for fir-wood lignin have been suggested. Thus the Glasser model [39] for lignin with molecular weight > 17 000 contains 94 phenol–propane units and takes into account most of the known analytical data. The results of simulations of the lignin structure (models suggested by Glasser,[39] Erickson [40] and Nimz [41]) are presented in Table 1.

The structural heterogeneity of lignins is associated with specific features of lignin biogenesis in wood tissues. The first stage of lignin biosynthesis is the enzymic oxidative deprotonation of *p*-hydroxycinnamyl alcohols (coumaryl, coniferyl and sinapyl alcohols) leading to the formation of a system containing the radicals **1a**–**e** (Scheme 2).[38]

Scheme 2



Recombination of two radicals affords one of 36 possible dimers. Upon the action of peroxidases, the latter undergo further oxidation producing dimeric radicals which, in turn, can form several hundred combinations of tetramers. The random character of the electron localisation predetermines the sporadic character and irregularity of the lignin structure.[3,5]

However, not all combinations in the coupling of monomers are of the equal probability. It has been shown by quantum-chemical calculations that the electron density distribution favours the formation of the ether C(β)–O–C(4) linkage resulting from the coupling of radicals **1a** and **1b**. Indeed, this linkage type predominates in lignins (Table 1). The functional group distribution with regards to the linkage types for the C(α), C(β) and C(γ) atoms in the side chain is described by the Ridholm diagram [38] (Table 2). Thus, the literature data available to date do not provide an unambiguous definition of lignin as an individual chemical compound and this substantially prevents assessment of its reactivity by the methods of classical organic chemistry, *i.e.*, by studying reactions of simple monomers and dimers mimicking different substituted phenol–propane structural units of lignin. Such studies may only provide helpful information regarding the elementary reactions of the lignin functional groups with oxidants rather than predict unambiguously their reactions with lignin itself.

The residual lignin in sulfate pulp from *Pinus radiata* has been studied by means of mass spectrometry and ^{13}C NMR spectroscopy.[36] Residual lignin was isolated by treating the sulfate pulp with cellulase. As the duration of sulfate cooking is increased, the number of the C–C bonds increases and the portion of the β-aryl-ether bonds in the residual lignin is decreased, thus indicating the higher degree of lignin condensation. Despite the reduction of a

Table 2. Functional group distribution in lignin according to bond types based on ^{13}C NMR spectroscopic data (the Ridholm diagram).

Group	Structural unit [a]		Proportion
C(γ)–OH	coniferyl alcohol type		0.04
C(γ)–OH	dihydroconiferyl alcohol type		0.03
C(γ)–OH	guaiacylglycerol type		0.02
C(γ)–OH	other primary alcohols		0.60
C(γ)=O	coniferyl aldehyde type		0.03
C(γ)–O–C(α)	pinoresinol, phenylisochroman, open-type units		0.18
C(γ)–O–C(4)	ether group		0.02
C(γ)H_3	methyl group		0.04
C(γ)H_2	γ-lactone (ring 14a)		0.02
C(γ)=O	the same (ring 13a)		0.02
		total	1.00
C(β)–O–C(4)	general type		0.44
C(β)–C(5)	the same		0.14
C(β)–C(6)	"		0.04
C(β)–C(β)	"		0.14
C(β)–C(1)	"		0.10
C(β)–C(α)	coniferyl alcohol and coniferyl aldehyde type		0.07
C(β)H_2	coniferyl alcohol type		0.03
C(β)–OH	guaiacylglycerol type		0.04
		total	1.00
C(α)–OH	coupling of rings 12–15; C(β)–C(1) bonds; guaiacylglycerol type		0.25
C(α)=O	keto group		0.06
C(α)=O	aldehyde group		0.11
C(α)–O–C(γ)	pinoresinol, phenylisochroman, open-type units		0.20
C(α)–O–C(4)	coupling of rings 17–18		0.11
C(α)–C(β)	coniferyl alcohol and coniferyl aldehyde type		0.07
C(α)H_2	dihydroconiferyl alcohol type and others		0.06
C(α)–O–C(4)	general type, *e.g.*, in coupling of rings 3–4		0.10
C(α)–O–	bonds with carbohydrates and others		0.04
		total	1.00

[a] For structural units and ring numbers, see Scheme 1.

Table 3. Functional group content in LMP and sulfate lignin.[18]

Functional groups	Number of groups per 100 phenol–propane units		Method of analysis
	fir-wood LMP [a]	pine-wood sulfate lignin [b]	
OH (total amount)	120	120	acetylation
guaiacol type	30	60	oxidation with KIO_4
catechol type	—	12	reaction with Fe^{2+}, calorimetry
aliphatic	90	48	see footnote [c]
COOH	5	16	methylation
CO (total)	20	15	treatment with $(NH_2OH)\cdot HCl$, volumetry, KBH_4
coniferyl aldehyde type	3	—	reduction, $\Delta\varepsilon_i$-method [d]
α-CO	7	5	the same
β-CO and others	10	10	see footnote [c]

[a] Molecular formula for a structural unit of fir-wood LMP is $C_9H_{8.8}O_{2.4}(OCH_3)_{0.96}$. [b] Molecular formula for a structural unit of pine-wood sulfate lignin is $C_9H_{7.9}O_{2.1}S_{0.1}(OCH_3)_{0.82}$. [c] Calculated by difference. [d] Method of differential UV spectroscopy based on the measurement of a difference in absorption of compounds with ionised and non-ionised phenolic and hydroxy groups in solutions of different pH.[12]

percentage of the β-aryl-ether bonds in lignin from 70% to 50%, the portion of these bonds in the residual lignin remained to be considerable even in the cases of low lignin content in pulp upon profound delignification. The sulfate lignin differs from slightly modified lignin of mechanical pulps (LMP) in the content of functional groups (Table 3).

The sulfate pine-wood lignin contains fewer carbonyl and aliphatic hydroxy groups and more carboxy and phenolic OH groups.[1–3] It is free from the coniferyl–aldehyde groups, which are lost during the sulfate cooking,[42] and virtually free from the benzyl alcohol OH or ether groups. During the sulfate cooking partial loss of the γ-hydroxymethyl and methoxy groups is also observed. In addition, contrarily to LMP, sulfate lignins contain the thiol group and elementary sulfur.[8,42]

Softwood lignins are mostly built up of guaiacol derivatives, while guaiacol and syringol derivatives are the main constituents of hardwood lignins. Thus non-fractionated sulfate birch-wood lignin contains approximately equal amounts of both types of derivatives.[36] The fractionation of lignin has shown that the ratio of syringol and guaiacol derivatives is increased from 0.8 to 1.5 with diminishing of the lignin molecular weight from 3500 to 650.[29]

Examination of DHP has shown that these compounds have different structures and properties depending on the manner of addition of initial monomers (substituted phenol–propane units) to the reaction mixture. When the monomer is added in one portion, the couplings of dimeric radicals with a monomer occur more rarely than in the gradual addition, whereas the couplings of a 'monomer–monomer' type become more abundant. In this case, the C(β)–C(5) bonds predominate.[15] The probability of the radical coupling of a 'polymer–polymer' type is higher on gradual addition of the monomer due to the low concentration of the latter. In this case, the C(β)–O–C(4) bonds predominate. It should be noted that recent hydrodynamic investigations of DHP and slightly modified softwood lignins do not quite agree with this hypothesis of the existence of two types of lignins.[2]

The native lignin is synthesised in plants from monomeric molecules that usually have from two to four functional groups.[15,28] The formation of both branched chains and network structures (at gel-point) is theoretically possible.[24] As has already been pointed out, the interaction of the growing lignin polymeric chains with surrounding macromolecules of non-cellulosic polysaccharides in plant tissues results in the formation of an amorphous lignocellulosic matrix. According to the Erin'sh hypothesis,[7,26] the three-dimensional structure of this matrix represents a superposition of three networks, *viz*., a network of hydrogen bonds between lignin and carbohydrates (H-network), a network of the lignin–carbohydrate bonds (LC-network) and a network of lignin itself. The most important arguments in favour of this hypothesis are insolubility of native lignin in all neutral solvents without preliminary chemical or mechanical treatment and high polydispersity of lignins isolated from wood tissues. Based on the theory for branching processes, the average molecular masses for sol fractions of model lignin compounds have been calculated [30] to be 1300–13 800. According to these values, the lignin extracted with ethanol in the absence of catalysts can be considered as a sol fraction of the native lignin. A new promising direction in the study of biosynthesis and the structure of lignin is a computer-assisted simulation of the growth of fractal clusters with fractional dimentionalities.[24]

Thus the currently available results of direct and indirect chemical, physicochemical and physical investigations taken altogether do not allow one to define unambiguously the formula and all levels of structural organisation for lignin. The properties and reactivities of industrial lignins depend to a considerable extent on the preparation methods.[1,17] The residual lignin is the most condensed and high-molecular-weight part of the lignin matrix involved into a lignin–cellulose composition, and its selective removal from cellulose fibres can only be achieved with the use of oxidants.[43] The presence of different types of functional groups and bonds in sulfate lignin and in the residual one predetermines a wide range of reagents used for lignin oxidative destruction in the preparation of cellulose from raw wood materials.

The main method for the study of lignin transformations is based on the analysis of reaction products resulting from the reaction of model compounds with oxidants. The most efficient reagent used for oxidative destruction and solubilisation of residual lignin in the pulp bleaching are molecular chlorine,[44–46] sodium hypochlorite,[47–49] hypochlorous acid,[48,50] sodium chlorite,[50] chlorine dioxide,[51,52] organic [9,10,53] and mineral [54] peroxy acids, hydrogen peroxide,[55–57] oxygen [58,59] and ozone.[60–62] One of promising approaches to oxidative destruction of residual lignin in industrial pulps during bleaching is the biotechnological method.[63,64]

Molecular chlorine is widely employed in the pulp industry for oxidation of lignin during the pulp bleaching, however, its application is accompanied by concomitant formation of a number of toxic aromatic chlorine-containing products,[65,66] including dioxins.[67] The use of sodium hypochlorite for the pulp bleaching is accompanied by the formation of chloroform.[68] Chlorinated hydrocarbons are dangerous for both living organisms and the Earth ozone layer. Therefore, the oxidation processes based on the use of environmentally safer reagents, such as hydrogen peroxide, chlorine dioxide and ozone, are of great importance. The reactions of model lignin compounds with these reagents are discussed below.

III. Oxidation of model compounds

1. Oxidation with hydrogen peroxide and oxygen

In an alkaline medium, hydrogen peroxide can undergo various transformations. When the concentration of a base is high, the decomposition of H_2O_2 follows predominantly a radical mechanism with the formation of molecular oxygen:[69,70]

$$H_2O_2 + 2OH^- \longrightarrow O_2^{2-} + 2H_2O, \quad (1)$$

$$O_2^{2-} + H_2O_2 \longrightarrow O_2^{-\bullet} + {}^{\bullet}OH + OH^-, \quad (2)$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O, \quad (3)$$

$$O_2^{-\bullet} + H_2O \longrightarrow HO_2^{\bullet} + OH^-, \quad (4)$$

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2. \quad (5)$$

The oxidation of lignin with oxygen in an alkaline medium is accompanied by generation of the radical anions $O_2^{-\bullet}$, hydroxyl radicals and singlet oxygen ($^1O_2$). The schemes of generation of the reactive oxygen forms and their mutual transformations are described by the following equations

$$^{\bullet}O_2^{\bullet} + e^- \rightleftharpoons O_2^{-\bullet}, \quad (6)$$

$$O_2^{-\bullet} + H^+ \rightleftharpoons HO_2^{\bullet}, \quad (7)$$

$$O_2^{-\bullet} + HO_2^{\bullet} \longrightarrow HO_2^- + {}^1O_2, \quad (8)$$

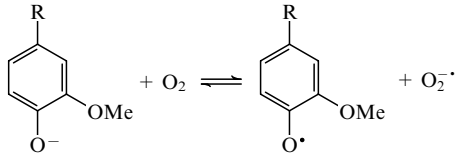
$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + {}^1O_2, \quad (9)$$

$$HO_2^- + H_2O_2 \longrightarrow O_2^{-\bullet} + HO^{\bullet} + H_2O, \quad (10)$$

$$2\,(^1O_2) \longrightarrow 2\,O_2 + h\nu. \quad (11)$$

Comparison of these equations with the equations (1)–(5) shows that both systems contain all the above-mentioned species independently of the oxidant used (O_2 or H_2O_2).[70,71] The equations (8), (9) and (11) account for the chemiluminescence observed in the oxidation of lignin with oxygen.[71–73] The decomposition of H_2O_2 is catalysed by transition metal ions (Fe, Mn, Cu, Zn, *etc.*) that are present in plant tissues and lignin.[59,74,75]

The rate and the depth of the lignin oxidation with H_2O_2 and O_2 depends on the reaction conditions. The reaction (6) leads to the single-electron oxidation of a phenolic fragment in lignin.

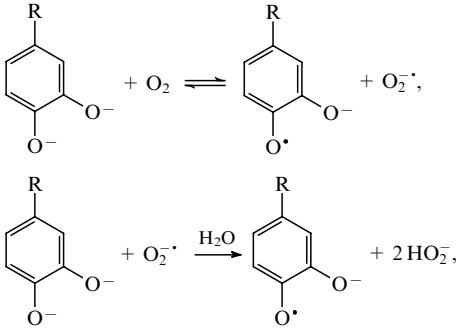


(12)

The superoxide radical anion $O_2^{-\bullet}$ takes part in the single-electron transfer as a reducing agent and in nucleophilic deprotonation [equation (7)] and substitution reactions. In aqueous and non-aqueous media, this radical anion can oxidise hydroquinones[53] and aromatic dianions.[69,70] Vanillin, acetovanillone and guaiacol are resistant to the action of the radical anion in aprotic (pyridine, DMSO) solvents, while α-methylvanillyl alcohol is rapidly oxidised by this oxidant to acetovanillone and hydroquinone is oxidised to acids.[76] Despite the oxidation of some model compounds, the sulfate lignin itself does not undergo any noticeable changes except the partial loss of the phenolic hydroxy groups (according to the data of liquid chromatography, ^1H NMR, IR and UV spectroscopy).[77–79]

The hydroxyl radical $HO^{\bullet}$ acts as an electrophile to form σ-complexes with aromatic structural units of lignin. The latter undergo subsequent transformations involving cleavage of the side-chain C–C bonds of lignin, cleavage of the aryl–aryl bonds and demethylation.[80,81] The radicals $HO^{\bullet}$ also induce lignin hydroxylation, cleavage of biphenyl bonds and degradation of aromatic rings.[43] In this respect, these radicals are more reactive than $O_2^{-\bullet}$. On the contrary, in reactions with carbonhydrates,[71–73] the radical $HO^{\bullet}$ is less reactive: its addition to the aromatic fragments of lignin occurs fivefold faster than hydrogen abstraction from carbohydrates. Unlike $HO^{\bullet}$, the superoxide radical anions react with lignin with difficulty but easily destroy cellulose.[70] This apparently is a result of a different ratio of the nucleophilic and electrophilic reactive centres in lignin and carbohydrates.

It was found[70] that lignin and catechol are readily oxidised at pH 14 with hydrogen peroxide even at room temperature producing the radical anions $O_2^{-\bullet}$. The latter are detected by the appearance of an intense violet colour in the presence of Tetrazolium Violet 1–2 min after the beginning of the reaction. Such model compounds as guaiacol, isoeugenol, vanillic and ferulic acids, β-guaiacyl ether of α-guaiacylethanone and β-guaiacyl ether of α-guaiacylethanol did not react with H_2O_2 even at 60 °C for 4 h. An important practical outcome of this study was the finding that catechol and the Pepper lignin do not virtually undergo oxidation at pH ⩽ 11.0. On increasing pH to 12.25, the rate of the catechol oxidation is sharply increased, which is rationalised[70] as the result of the second-step dissociation of catechol ($pK_a \sim 12.5$, for the first step $pK_a = 9.45$). Kinetic studies provide evidence on an induction period prior to the appearance of H_2O_2 in the system, which catalyses the process described by the following equations



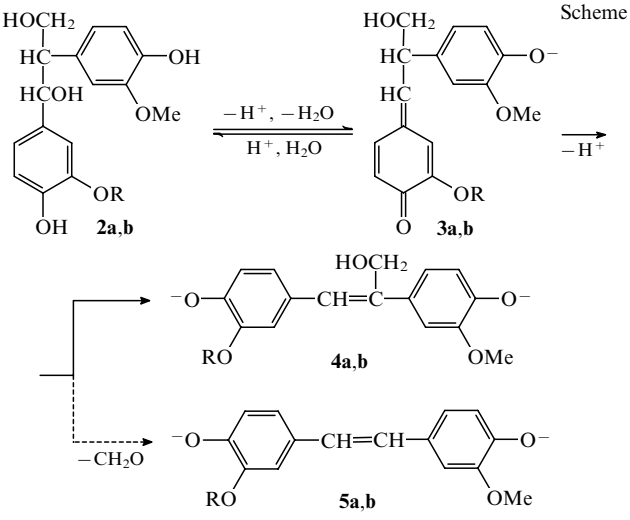
$$HO_2^- \overset{H_2O}{\rightleftharpoons} H_2O_2 + OH^-,$$

$$HO_2^- + H_2O_2 \longrightarrow O_2^{-\bullet} + HO^{\bullet} + H_2O.$$

Thus, at high concentration of a base (NaOH), low content of oxygen and moderate temperatures the most probable reaction centres in lignin are the catechol structural units, and hydrogen peroxide acts on lignin in the same manner as does oxygen.

The oxidation of dimeric model lignin compounds of the 1,2-diarylpropane-1,3-diol type with hydrogen peroxide and oxygen has been studied[79] in the example of 1-(4-hydroxy-3-methoxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol (**2a**) and 1-(3-ethoxy-4-hydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol (**2b**). It was preliminarily shown that compound **2b** forms 3-(3-ethoxy-4-hydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-ol (**4b**) and 3-ethoxy-4,4′-dihydroxy-3′-methoxystilbene (**5b**) (side reaction) dianions at pH 11–13 in the absence of oxygen (in vacuum), the equilibrium mixture containing *ca.* 95% of the initial dimer (Scheme 3).

Scheme 3



R = Me (**a**), Et (**b**).

Analogous stilbene derivatives were earlier[80,81] obtained from diols of the type **2a**,**b**. However, the α,β-elimination products are formed in higher yields only in the case of structures containing hydroxymethylphenyl fragments.[82]

Vanillin and ethylvanillin instead of stilbene dianions **4b** and **5b** were obtained in experiments with preliminary passage of air or

nitrogen through the system, thus indicating the oxidative character of the process. This result can be explained by rapid autooxidation of the initially formed stilbenes with a trace amount of oxygen dissolved in the alkaline solution.

The oxidation of diol **2b** with a solution of H_2O_2 stabilised at pH 10.5 results in the formation of ethanol, methanol ethylvanillin and small amounts of other compounds (the conversion of the initial diol is 30%) (Table 4). After 4 h of the treatment, 85% of hydrogen peroxide still remained unconsumed. Some amount of H_2O_2 is lost due to decomposing, and about 1%–2% of the oxygen thus generated is consumed in the oxidation of diols as follows from the analysis of stilbene and the initial diol autooxidation products.

Diols of the type **2** are less reactive towards H_2O_2 than the products of their initial oxidation.[79] According to the composition of the oxidation products, the main direction of the oxidation of these diols with the stabilised hydrogen peroxide (*i.e.*, in an oxygen-free system) involves the nucleophilic attack of the HO_2^- anions on quinonemethide anion **3** and the oxidation of stilbene dianion **4**. The hydroperoxide thus formed undergoes consecutive rearrangement and fragmentation yielding the hydroquinone dianion (**6**) and α-(4-hydroxy-3-methoxyphenyl)-β-hydroxypropanol anion (**11**). The latter is converted into the guaiacylglycol anion (**8**) (Scheme 4).

The oxidation of phenylpropan-2-one with hydrogen peroxide follows the same mechanism, this reaction may be regarded as an alkaline analogue of the Baeyer–Villiger reaction.[82] It should be noted that dihydroxyphenyl derivatives, like guaiacylglycol, have also been obtained by the action of basidiomycetes *Phanerochaete chrysosporium* on diols of the type **2**.[83] The same mechanism for conversion of α-hydroperoxide into guaiacylglycol and ethylvanillin has been proposed in another study.[84]

The mechanism of oxidation of stilbenes **4b** and **5b** with hydrogen peroxide in alkaline media in the absence (or virtual

Scheme 4

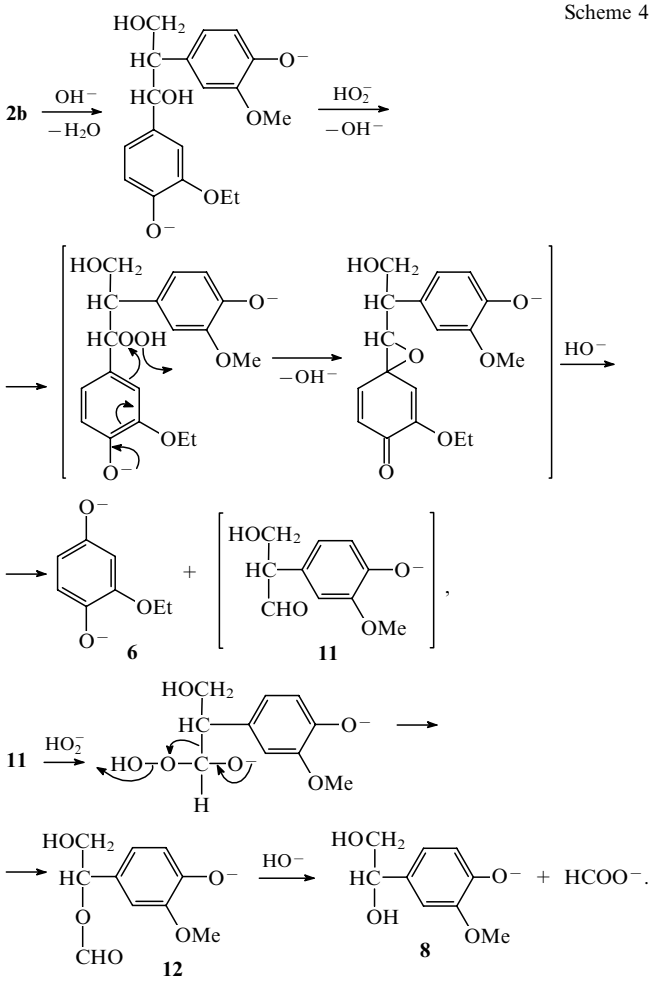


Table 4. Oxidation products of the diol **2b** in a stabilised solution of hydrogen peroxide (*A*), with hydrogen peroxide in the absence of a stabiliser (*B*) and with atmospheric oxygen (*C*).[70]

Component of the reaction mixture	Yield (with respect to the theoretical one) (mol. %)		
	A [a]	*B* [b]	*C* [c]
1-(3-Ethoxy-4-hydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol (**2b**)	70	31	14–18
Ethoxyhydroquinone (**6**)	traces	~1	0
Ethylvanillic acid [d]	"	4	0
Ethylvanillin (**7**)	6–7	~14	60
Guaiacylglycol (**8**)	2	4	7.5
ω-Hydroxyacetoguaiacone (**9**)	0	2	traces
Methoxyhydroquinone	–	–	"
1,2,4-Trihydroxybenzene (**10**)	–	3.5	0
Methoxy- and ethoxybenzoquinones	–	traces	1–2
3-(3-Ethoxy-4-hydroxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)prop-2-en-1-ol dianion (**4b**)	0	–	–
3-Ethoxy-4,4′-dihydroxy-3′-methoxystilbene dianion (**5b**)	1	–	–
Methanol	15	29	36
Ethanol	7	17	4–5
Residual H_2O_2	85	5	–

[a] Reaction conditions: 45 °C, 4 h, pH 10.5, [dimer] = 0.07×10^{-3}, [DTPA] = 0.4×10^{-3}, [$MgSO_4$] = 0.16×10^{-3} mol litre^{-1}, [H_2O_2]/[dimer] = 3. [b] Same reaction conditions but without addition of DTPA and $MgSO_4$. [c] Reaction conditions: 45 °C, 4 h, pH 10.5. [d] Hydroxyethylvanillin in the case of the method *B*.

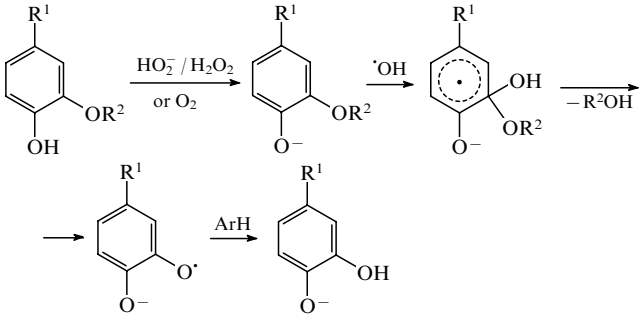
absence) of oxygen is rather difficult to describe in detail since the hydroperoxide anion, as a strong nucleophilic reagent, cannot directly attack the electrophilic alkene structures. The oxidation occurs as the result of preliminary rearrangement of the stilbene dianion **4b** into quinonemethide and subsequent attack by the hydroperoxide anion. ω-Hydroxyacetoguaiacone, ethoxyhydroquinone and acetoguaiacone were expected to be the products of these reactions. However, only a trace amount of ethoxyhydroquinone has been detected (Table 4). Thus, the reaction of non-dissociated hydrogen peroxide with the stilbene **4b** seems to be more probable.[79]

Comparison of the results of oxidation of the diol **2** with a non-stabilised alkaline solution of hydrogen peroxide at constant pH 10.5 with those obtained in its oxidation with stabilised H_2O_2 in the absence of oxygen (Table 4) allows one to reveal a number of differences, *viz.*, the decomposition of non-stabilised hydrogen peroxide is almost complete, the degree of conversion for the initial diol is increased from 30% to 69%, the yields of the oxidation products (especially of ethanol, methanol, ethylvanillin and alkoxyhydroquinone) are higher, and the products contain the following organic acids:[70]

Acid	Yield (%)
Succinic	⩽ 1
Oxalic	⩽ 1
Hydroxymaleic	1–2
Malonic	5
Glycolic	1–2

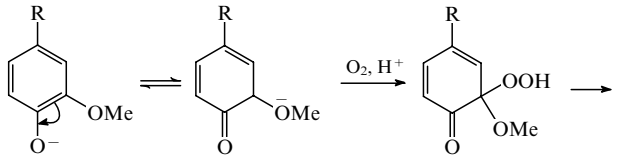
These differences are explained by the presence in the reaction mixtures of some additional oxidants: oxygen, hydroxyl radicals and superoxide radical anions along with non-stabilised hydrogen peroxide, which are formed in the reactions (1)–(4). In the other

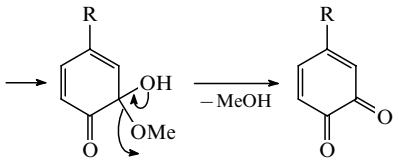
words, the oxidation process induces the generation of new oxidants.



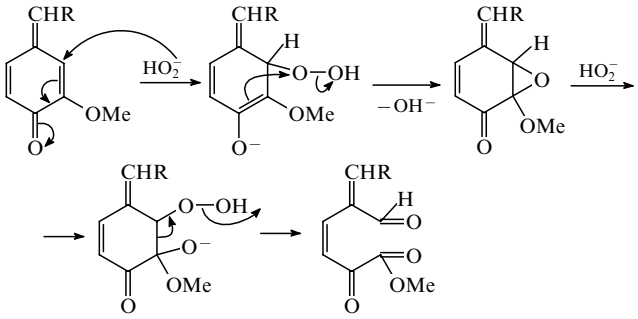
R^1 = OH, OAc; R^2 = Me, Et.

The action of oxygen generated upon decomposition of hydrogen peroxide results in the formation of quinoid products.



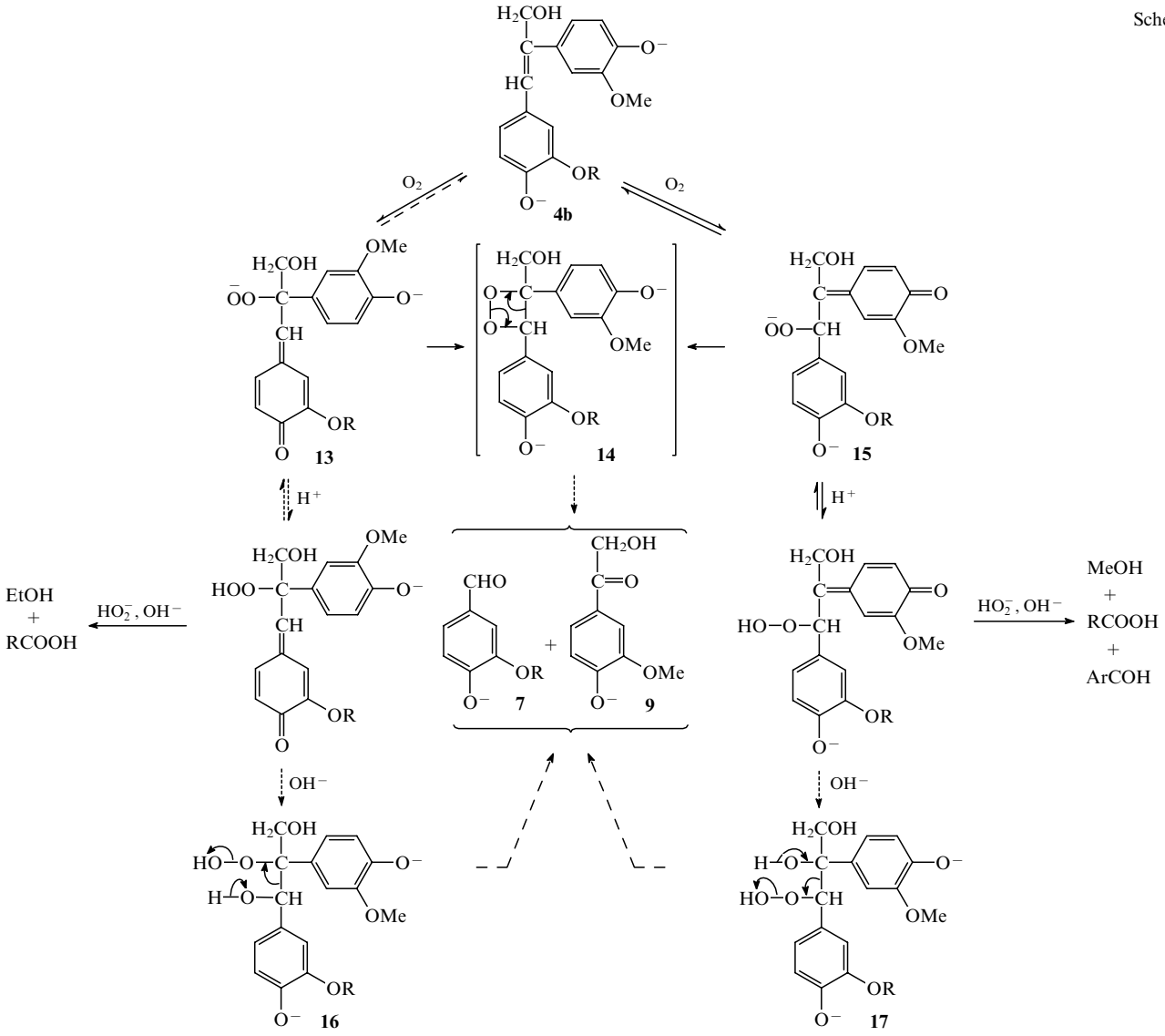


Quinonemethides of the type **3** and *o*-quinones which appear in the reaction mixture are oxidised by hydroxyperoxide anions to carboxylic acids.



When the diol **2b** is allowed to react with H_2O_2 in the absence of a stabiliser and without maintenance of pH at 12.5, the pH value is decreased to 10 due to the accumulation in the reaction

Scheme 5



mixture of carboxylic acids. Simultaneously, there is observed an increase in the portion of nonconsumed diol and an increase in the total yield of ethylvanillin and ethoxyhydroquinone (from 15% to 29%) as a consequence of the increased concentrations of hydroperoxide anion and non-dissociated hydrogen peroxide in the solution.

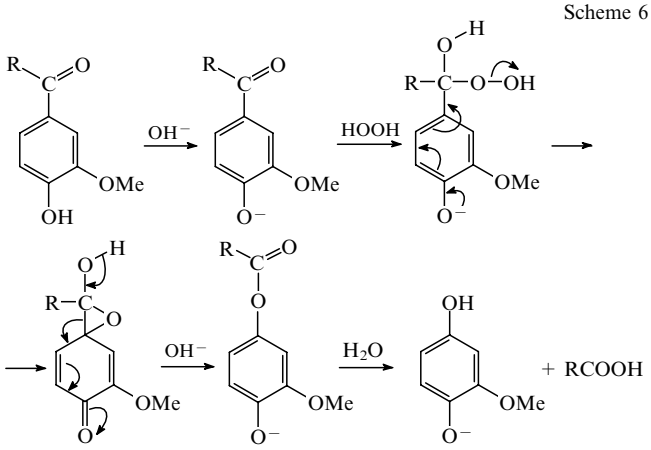
The particular contribution of oxygen generated *in situ* in the total oxidation process was estimated in the oxidation of the diol **2b** with molecular oxygen, which allowed the authors [79] to propose a more detailed mechanism for this reaction (Scheme 5), which takes into account the published data.[80,81] As has already been shown, the diols **2a**,**b** are partially converted in alkaline media into the stilbene dianions **4** and **5**, which undergo intense oxidative destruction with oxygen. According to the much higher yield of methanol compared with that for ethanol, the reaction predominantly proceeds by a pathway involving the intermediate formation of hydroperoxide **15**.

The data considered above show that model structures like **2a**,**b** have low reactivity towards hydroperoxide anion but can be relatively easily oxidised with oxygen to low-molecular-weight products. In the presence of hydrogen peroxide, stabilisers, and at pH $\leqslant$ 10.5, the main oxidising reagent is the hydroperoxide anion, whereas molecular oxygen and its other reactive forms, *i.e.*, $O_2^{-\bullet}$, O_2^- and $^\bullet OH$, become the major oxidants upon increase in pH to 12.

Alkaline hydrogen peroxide readily oxidises α,β-unsaturated ketones of the coniferyl aldehyde type and α,β-diketones but not α-ketones with an etherified phenolic hydroxy group, nor (virtually) propioveratrone and α-hydroxypropioveratrone.[79]

α-Ketones are oxidised through addition of the hydroperoxide anion to the electrophilic carbon atom of the carbonyl group with the intermediate formation of a quinoid compounds. Following recovery of the aromatic system, an ester is formed, which is then hydrolysed. The products of such reactions are vanillyl alcohol and a carboxylic acid with the same aliphatic radical as in the initial ketone [82] (Scheme 6).

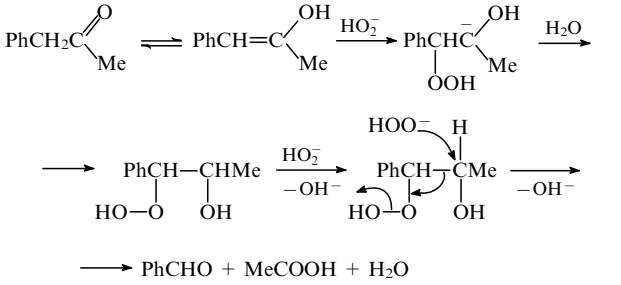
Scheme 6



In the case of model compounds of the general formula $ArCH_2C(O)Me$, the intermediate formation of enolic tautomers is observed.[10] An investigation of the oxidation of a series of ketones bearing different subsituents in the positions 3 and 4 of the benzene ring has shown [82] that these reactions mainly result in the rapid cleavage of the initial phenylpropan-2-one into benzaldehyde and acetic acid (Scheme 7).

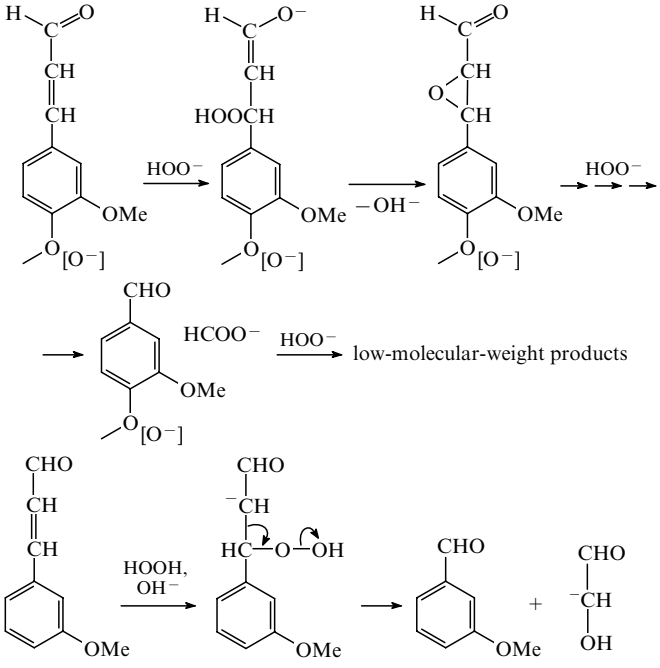
The mechanism of these reactions apparently involves an attack by the hydroperoxide anion of an enolic tautomer on its C(α) atom and an intermediate formation of β-hydroxyhydroperoxide anion, fast protonation of this anion by water and subsequent attack by the hydroperoxide anion on the C(β) atom of the initial carbonyl group, leading eventually to synchronous cleavage of the O—O bond in the intermediate organic peroxide

Scheme 7



and the C(α)—C(β) bond. The oxidation of α,β-unsaturated ketones of the coniferyl aldehyde type to benzaldehyde occurs *via* the corresponding hydroperoxides and epoxides (Scheme 8).

Scheme 8



The reactions of the hydroperoxide anions with quinoid structures result either in the ring opening or in the splitting off of the side chains (Scheme 9).[8,85] In the oxidation of methoxy-substituted quinones, the demethoxylation and formation of methanol were also observed.

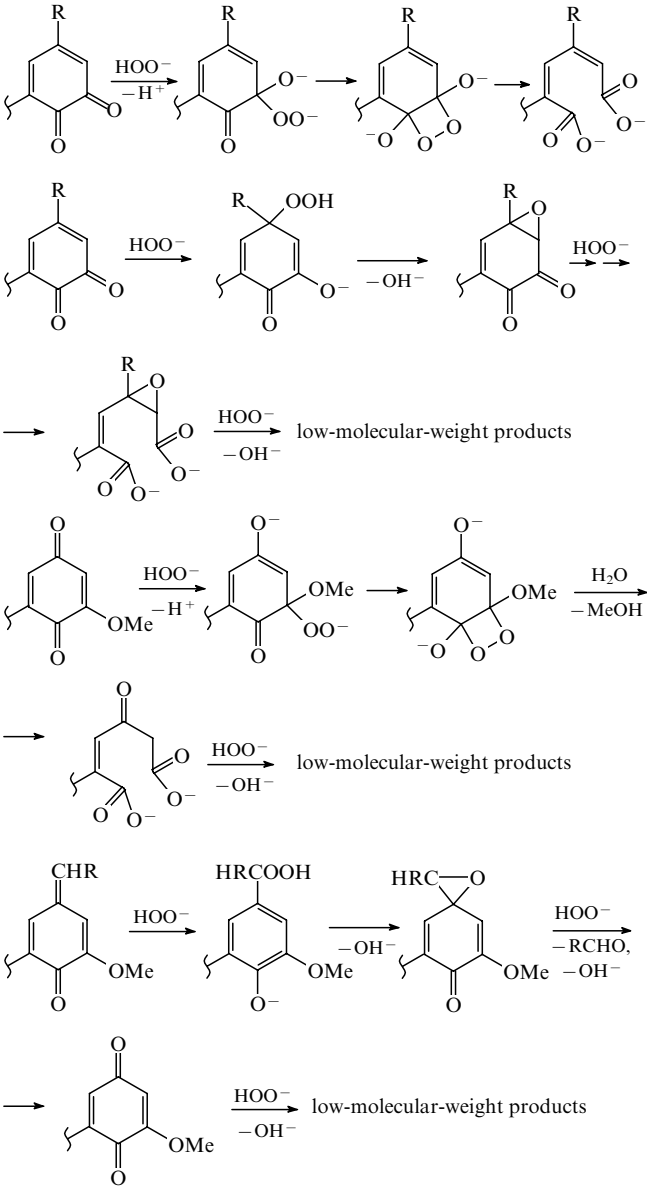
The oxidation of the quinone rings represents apparently a longer reaction pathway in lignin oxidative destruction, even if decomposition of non-terminal units is considered. This requires a larger amount of an oxidising reagent for the scission of the carbon chains than for the side-chain oxidation.

An important feature of the reactions shown in Schemes 6–9 consists in participation of the hydroperoxide anion as a reactive nucleophilic species, which reacts with electron-withdrawing (electrophilic) sites of lignin.

In an acidic medium, the mechanism of reaction of hydrogen peroxide with organic compounds is analogous to that of peroxy acids. In this case, either a protonated hydrogen peroxide $H_3O_2^+$ or a hydroxonium ion are those reactive electrophilic species which attack the aromatic structures.[10]

The oxidation of model lignin compounds with hydrogen peroxide and peroxy acids mainly results in the hydroxylation of the aromatic nuclei, oxidative demethoxylation, oxidative benzene ring opening, splitting off of the side-chains, cleavage of the C(β)—O ether bonds and formation of epoxides (Scheme 10).

Scheme 9

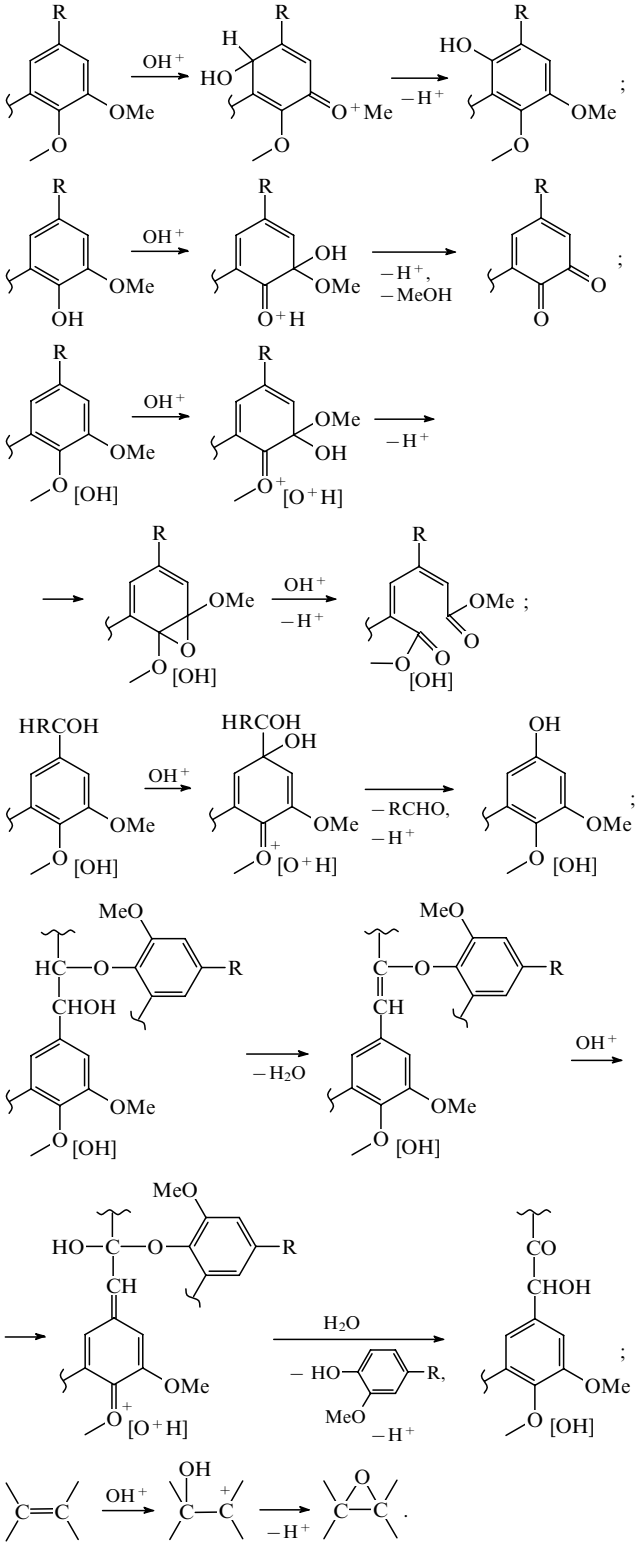


Salts of peracetic, performic and mono- and diperoxysulfuric acids in alkaline media are employed as the oxidants for oxidative delignification of wood tissues and mechanical pulps.[8–10,86–88] Under conditions favouring stabilisation of the peroxy anion, this acts as a nucleophilic reagent.

The oxidation of structures of the benzyl alcohol type with hydrogen peroxide and peroxy acids to ketones and aldehydes may follow the radical mechanism involving hydroxyl radicals.[8–10,85]

It should be noted that studies on the oxidation of compounds that mimic the lignin structural fragments are only useful in drawing a probable scheme (and in some cases, in elucidation of the mechanism) of reactions of the residual pulp lignin. In fact, the processes of oxidative destruction of the residual lignin under the action of a majority of peroxides do not go to completion (except for ozonolysis) and kinetic parameters determined for the oxidation of model compounds substantially differ from those observed during the lignin destruction in a polymeric lignocellulosic matrix.

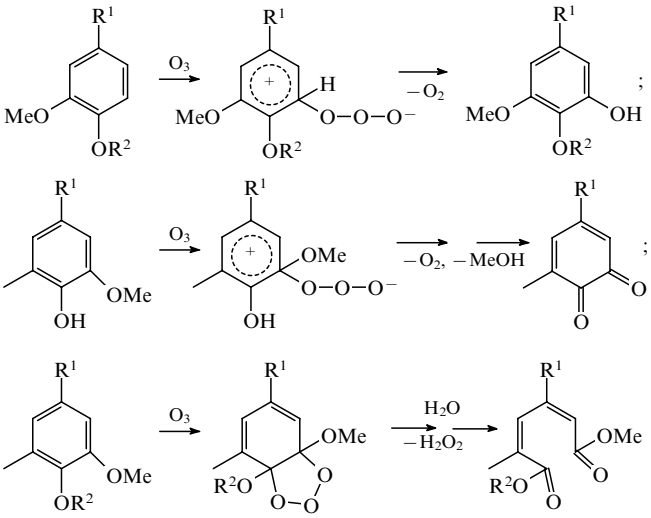
Scheme 10



2. Ozonolysis of model compounds

Reactions of ozone with organic compounds are widely used in organic synthesis, qualitative and quantitative analyses and chemical technology. The mechanisms of these reactions have been considered in detail.[89,90] In application to lignin, ozonolysis has been employed to prove its aromatic nature, to determine the nature of substituents in the aromatic rings[91] and to study the three-dimensional structure of side chains in the phenol–propane structural units.[92]

Scheme 11



R^1 = Alk, R^2 = H, Alk.

The first stage of the reaction of ozone with the aromatic fragments of lignin involves its electrophilic addition, and *o*-quinones or muconic acid derivatives (following ring opening) are the common final products of ozonolysis (Scheme 11).

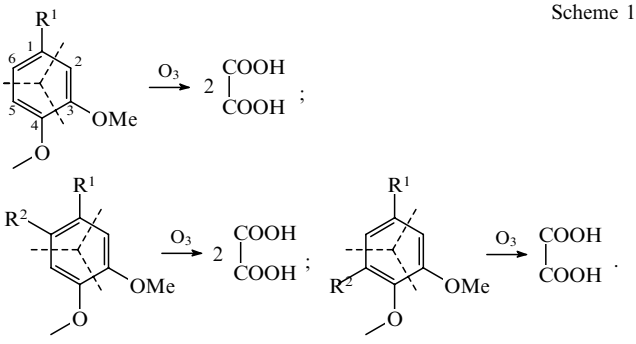
The ozonolysis of aromatic compounds is accompanied by the formation of strong oxidants, *viz*., oxygen, hydrogen peroxide, ozonides and trioxides, which react in an acidic medium with lignin as electrophiles.[89,90]

On comparison with monocyclic aromatic compounds, polycyclic derivatives react with ozone more readily, however, after incorporation of one or two molecules of ozone the rate of the process sharply decreases. Thus the reaction with naphthalene is stopped after addition of two molecules of ozone, and the reaction rate with phenanthrene is reduced by two orders of magnitude after the addition of the first molecule of O_3.[90]

In the preparation of ozone from oxygen, the concentration of the latter in the system is high, and all intermediate radicals are predominantly converted into the peroxide ones (according to EPR spectroscopy). These radicals are responsible for the chemiluminescence and chain oxidation of hydrocarbons.

The oxidation of alkenes, alcohols and ethers in the presence of ozone leads to the formation of carbonyl compounds; aldehydes are oxidised to carboxylic acids.[93] The cleavage of the C—H bonds occurs upon oxidation of oxygen-containing compounds.[90] Reactions with phenols predominantly proceed through the abstraction of the hydrogen atoms from the hydroxy groups, leading to the formation of phenoxyl radicals and subsequent aromatic ring opening. Based on the analysis of the final products, one can judge about the structure of a particular lignin elementary unit.[92–94] Thus the formation of two molecules of oxalic acid per guaiacyl fragment points either to the absence of aliphatic substituents in the benzene ring or to its presence in position 6, while the formation of one molecule of the acid suggests the presence of a substituent in position 5 (Scheme 12).

Scheme 12



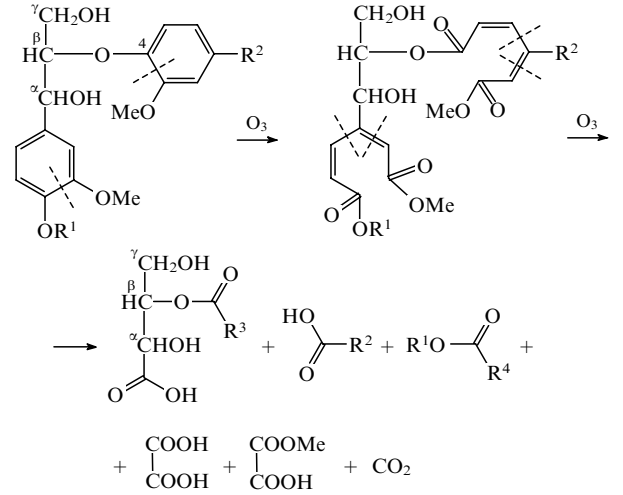
R^1 = R^2 = Alk, Ar.

It has been found[91] that preliminary reduction of lignin with sodium borohydride favours a higher yield of water-soluble acids upon subsequent ozonolysis. Obviously, the reduction of the constituent aldehydes, ketones and quinones simplifies the lignin structure and accelerates the oxidation process, which mostly affect the aromatic structures. However, sodium borohydride is rather expensive to be used for the industrial pulp bleaching.‡

The introduction of electron-withdrawing substituents, *e.g*., NO_2, Cl, *etc*., into a molecule of an unsaturated compound substantially reduces the rate of its oxidation with ozone due to a decrease in the electron density on the carbon atoms of the π-bonds.[90] This is quite important from the practical point of view, since pulp bleaching involves sequential treatment with various oxidants, including nitrogen oxides.[96]

Oxalic acid and its monomethyl ester, carbon dioxide and esters are the products of the oxidative destruction of the lignin C(β)—O—C(4) fragment[93] (Scheme 13).

Scheme 13



Thus ozone can react with virtually all types of the lignin structural units, including those condensed and linked to each other with carbon–carbon bonds, *e.g*., C(β)—C(1).[92]

An important point in the bleaching of sulfate pulp is that the depth, selectivity and rate of lignin oxidative destruction can be controlled by varying the functional composition of lignin using reduction, oxidation, *etc*.

Ozonolysis of lignin-containing technical pulp aimed at its bleaching results in the oxidative destruction of the residual lignin, which is accompanied by oxidation and destruction of polysaccharides and cellulose (the latter process is usually undesirable).[97] The accumulation of the carbonyl groups in the cellulose macromolecule reduces its chemical resistance, results in yellowing and enhances pulp destruction upon subsequent processing.

It is known that a decrease in the degree of polymerisation below a certain limit affects the durability of the paper products. The oxidative destruction of cellulose with ozone is a serious problem, which for a long time has been (and still is) an obstacle for the wide application of ozone in the pulp industry, together with the high cost of ozone and complexity of technological equipment for such processes.

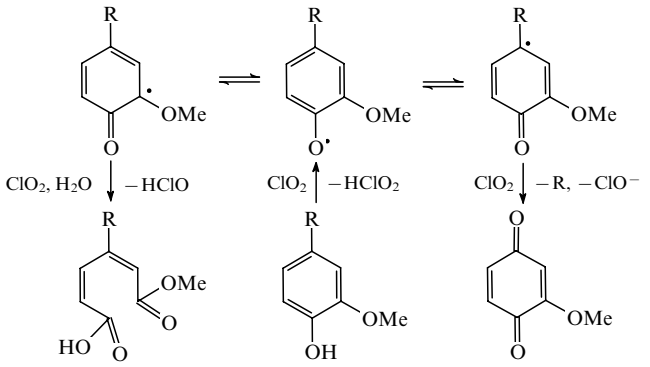
However, targeted destruction of polysaccharides, *e.g*., cellulose, chitin and chitosans,[98] is of particular interest for their conversion into the corresponding oligomers. In this case, the ozonolysis compares favourably in efficiency and ecological safety to other methods of oxidative destruction.

‡ The cost of 1 kg of $NaBH_4$ is approximately equal to that of all other chemicals consumed in the bleaching of 1 ton of a pulp.[95]

3. Oxidation of lignin with chlorine dioxide

Chlorine dioxide oxidises lignin in lignin–cellulose matrices without affecting cellulose. Lignin phenolic structural units are oxidised with ClO_2 upon abstraction of the hydrogen atoms from the phenolic hydroxy groups. Muconic acids and quinoid compounds are the final products of such reactions, which are formed without loss of the methoxy groups [99–101] (Scheme 14).

Scheme 14



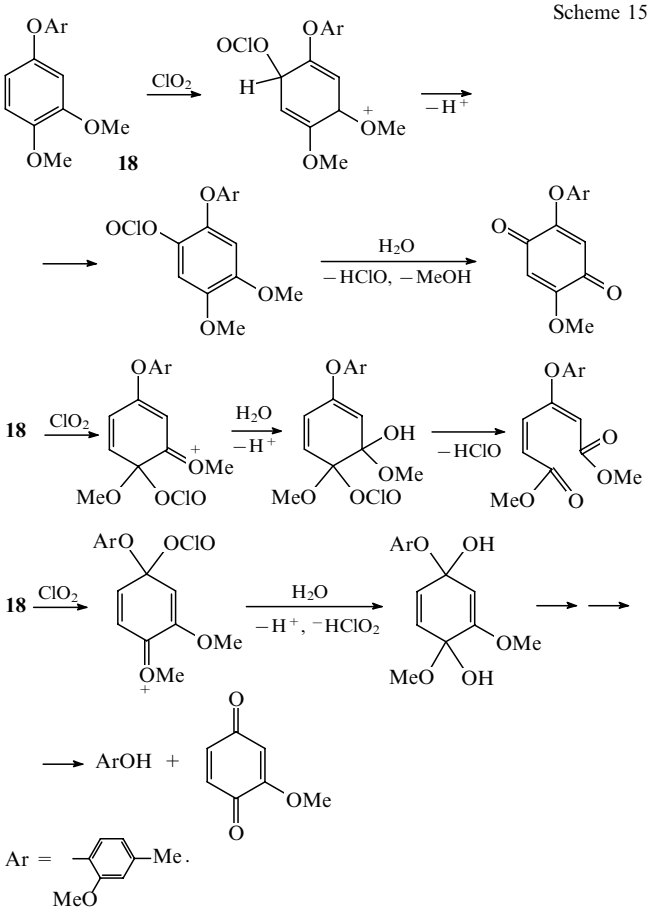
In the case of aromatic ethers, *e.g.*, 4-methyl-2,3′,4′-trimethoxydiphenyl ether (**18**), three different directions for the reaction with chlorine dioxide are possible.[99,100] These involve the formation of quinoid structures, opening of one of the aromatic rings and cleavage of the diaryl ether bond leading to the formation of hydroquinone and phenol derivatives (Scheme 15).

Veratryl β-guaiacyl ether (**19**) undergoes homolytic fragmentation under the action of chlorine dioxide, one of the reaction products being veratraldehyde. In parallel, the oxidative dehydrogenation of the α-hydroxy group occurs (Scheme 16).

The oxidation of 4,4′-dihydroxy-3,3′-dimethylstilbene (**20**), 4-hydroxy-3,3′,4′-trimethoxystilbene (**21**) and 3,4,3′,4′-tetramethoxystilbene (**22**) (the most common model compounds of native and residual lignins) with chlorine dioxide has been studied.[99–101] The main transformations of stilbenes **20**–**22** are shown in Scheme 17.

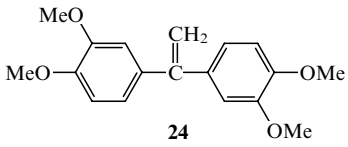
Yet another model compound of the residual lignin is 3,4-dimethoxy-β-(2-methoxyphenoxy)styrene (**23**). It reacts with chlorine dioxide by a similar mechanism (Scheme 18). The oxidation involves the formation of a complex of the oxidant with the π-electronic system of the alkene fragment.[101] In an acidic medium, this complex is protonated to form a resonance-stabilised radical cation and $HClO_2$. The addition of ClO_2 to the β-radical generated leads first to the chlorous ester (**A**), which is

Scheme 15

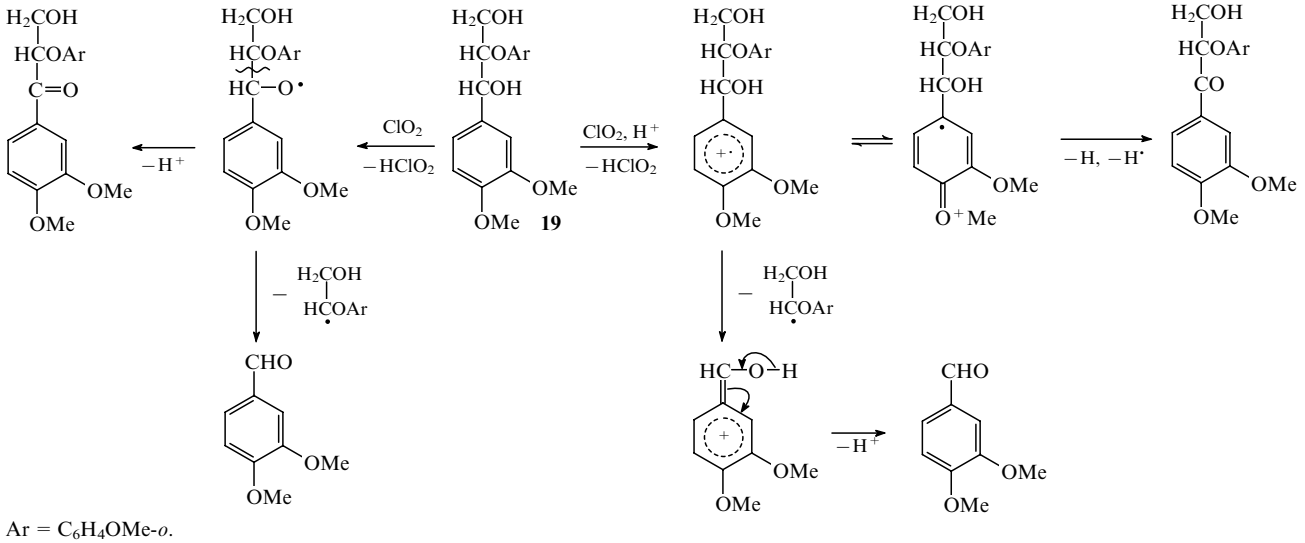


further converted into the ester **B**, from which aldehydes, ketones and esters are formed as the final products.

A possibility of the formation of 1,1-bis(3,4-dimethoxyphenyl)ethylene (**24**) from the corresponding stilbene as a result of aryl radical migration has been shown.[102]

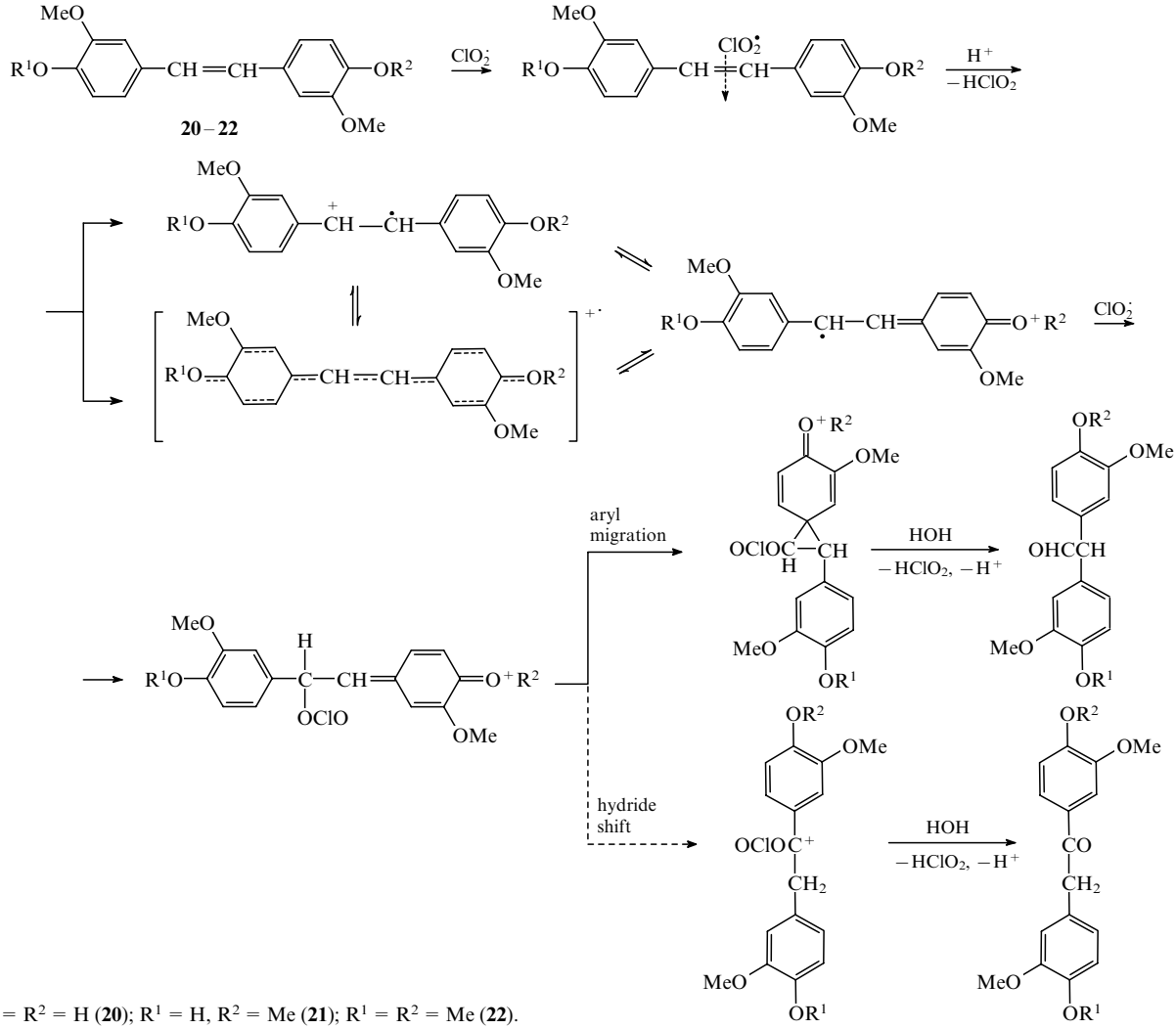


Scheme 16



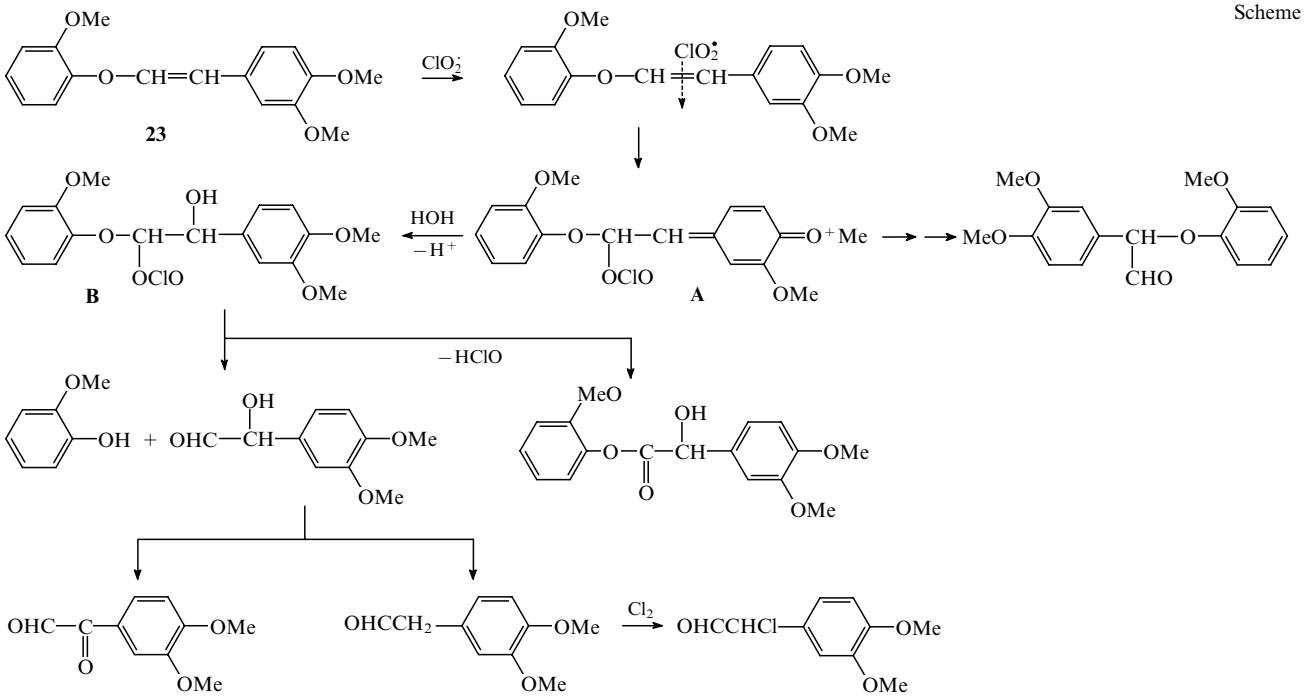
Ar = C_6H_4OMe-*o*.

Scheme 17



$R^1 = R^2 = H$ (**20**); $R^1 = H$, $R^2 = Me$ (**21**); $R^1 = R^2 = Me$ (**22**).

Scheme 18



Unlike stilbenes **20**–**23**, compound **24** does not undergo fragmentation under the action of chlorine dioxide. Among the reaction products, only mono- and dichlorinated derivatives have been found. Oxidative demethoxylation also takes place.

In general, the early stages of the reactions of model lignin compounds with chlorine dioxide result in the formation of conjugated carbonyl groups, *i.e.*, in new chromophoric groups and systems which, as has been shown earlier, are readily oxidised with hydrogen peroxide according to the ionic mechanism involving the nucleophilic addition of the hydroperoxide anion.

IV. Combined action of oxidants on the sulfate pulp lignin

As has already been mentioned, lignin remaining in the sulfate pulp after cooking represents the most condensed, and strongly bound to polysaccharides, part of modified natural lignin (residual lignin). Despite the fact that the composition (various combinations of bonds, functional groups and structural units) and three-dimensional (network [5, 7, 26] and fractal [22, 24, 25]) polymeric structure of lignin do not allow prediction of the degree and the rate of its oxidative destruction, analysis of the results of the studies on an oxidation of model lignin compounds with hydrogen peroxide, oxygen, ozone, chlorine dioxide and other reagents (*vide supra*) makes it possible to elucidate general features of this process.[8–10]

The reactivity of lignin towards oxidants depends on the nature of the reactant and the presence of nucleophilic and electrophilic sites in the lignin macromolecule. Under conditions of acid and base catalysis, each particular reagent can produce differently reacting species depending on the medium acidity. A classification of reagents [10] used for lignin oxidation according to their electron-donor and electron-acceptor properties (or nucleophilicity and electrophilicity, respectively) is given in Table 5. The mechanisms of their interaction with lignin and the reactivity of residual lignin itself substantially affect the rate and the depth of the sulfate pulp delignification and a number of the operation steps in pulp bleaching.

The oxidation of nucleophilic alkene fragments in lignin occurs as the initial addition of an electrophile followed by the attack of a nucleophile (Scheme 19).[10] The addition of electrophiles to lignin results in the appearance of new electrophilic sites in the lignin macromolecule and their activation towards the action of nucleophiles.

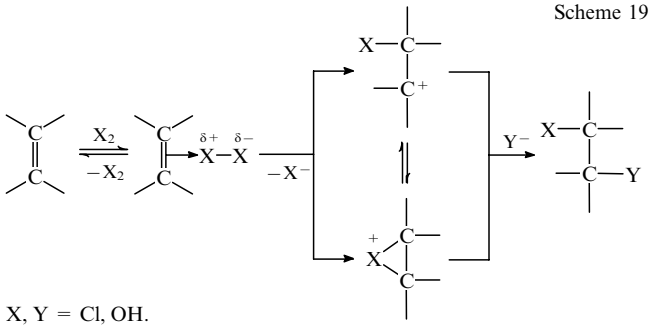
If one form of the reagent predominates and no cooperation exists between nucleophilic and electrophilic species, the rate of dissolution of the electrophilic reaction products of residual lignin is substantially decreased, which apparently leads to deceleration of the sulfate pulp delignification and to non-rational consumption of bleaching reagents in the chemicotechnological processes. The efficiency of the sulfate pulp delignification is especially low when such environmentally safe reagents as hydrogen peroxide and ozone are used compared to chlorine-containing reagents (Table 6).[103]

Normally, complete dissolution of the reaction products of lignin with electrophilic oxidants requires treatment with alkali, *i.e.*, the second stage in the pulp bleaching process is the treatment of pulps with a nucleophilic reagent (alkali). As a rule, Cl_2 + NaOH and O_3 + NaOH pairs are used for this purpose. In the second stage, some part of chlorine in chlorolignin is replaced by hydroxy groups, thus enhancing the hydrophilicity of the chlorinated lignin. Delignification of the sulfate pulp can be enhanced by applying 'oxidative alkalification', whereon oxidants such as sodium hypochlorite or hydrogen peroxide are added to an alkaline pulp solution.[104] The hypochlorite anion (ClO^-) acts on lignin as a nucleophilic reagent, while H_2O_2 in the absence of stabilisers and at high alkalinity of the medium generates various forms of oxidants:

$$H_2O_2 \longrightarrow O_2^{2-} \longrightarrow O^{-\bullet} + {}^{\bullet}OH \longrightarrow HO_2^{\bullet} \longrightarrow {}^1O_2.$$

The electrophilic mechanism predominates in the oxidation of lignin;[10, 15, 18, 105] this has earlier been shown for some lignin model compounds.[75–80]

Scheme 19



X, Y = Cl, OH.

Table 6. The depth of oxidative destruction of lignin in sulfate softwood pulps with equivalent amounts of different reagents.[95]

Reagent (conditions)	Oxidant consumption (% of the pulp mass) [a]	Depth of residual lignin oxidation [b]
Ozone	0.59	0.19
Hydrogen peroxide	1.26	0.30
Ozone + extraction with a NaOH solution	0.59	0.42
Sodium hypochlorite (pH 10)	2.63 [c]	0.53
Sodium hypochlorite + hypochlorous acid (pH 7.5)	2.63 [c]	0.64
Chlorine dioxide	1.00	0.67

[a] With respect to the reagent mass. [b] Corresponds to the degree of lignin conversion; the initial lignin content in sulfate softwood pulp is expressed as 76 permanganate units (1 p. u. is referred to the content of lignin in pulps according to Bjørkman, State standard 6845-54). [c] Per active chlorine unit (active chlorine is defined as an overall amount of chlorine-containing oxidants determined by iodometry).

Table 5. Reactive forms of the reagents, involved in pulp bleaching processes.

Process (medium)	Substrate	Reagent type	Reactive form	Reacting species	Number of electrons involved in the reaction
Oxidation (acidic)	aromatic and unsaturated structures	electrophile	cation	H^+, OH^+, O_3, Cl^+, NO^+, NO_2^+	2
			radical	$H^{\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet}$, $^{\bullet}O_2^{\bullet}$, $Cl^{\bullet}$, $ClO^{\bullet}$, $ClO_2^{\bullet}$, $NO^{\bullet}$, $NO_2^{\bullet}$	1
Reduction (alkaline)	non-conjugated and conjugated carbonyl compounds	nucleophile	anion	H^-, HO^-, HO_2^-, ClO^-, ClO_2^-, $S_2O_4^{2-}$	2
			radical	$H^{\bullet}$, e_{aq}, $SO_2^{-\bullet}$	1

Note. The list of reacting species includes both commercial bleaching reagents and the species that are not commercial bleaching reagents but can take part in various pulp bleaching processes.[9]

The most important characteristic of a delignifying reagent is the minimum content of lignin in pulp rather than the portion of lignin removed by this reagent from the pulp (bearing in mind that the initial content of lignin in pulps may vary) at which delignification with this reagent, taken in small excess, is terminated. According to this criterion, the reagents used for delignification of the sulfate pulp (after cooking) can be arranged in the following order: oxygen < hydrogen peroxide < chlorine (with subsequent extraction with a NaOH solution) < sodium hypochlorite < chlorine dioxide.[103]

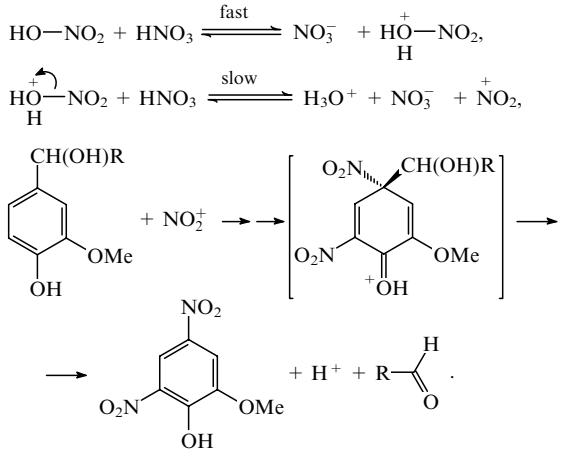
Lignin in industrial pulps (including sulfate pulp) cannot be selectively destroyed to give water-soluble products and completely removed from pulps by either of the oxidants. To achieve complete delignification (and concomitant bleaching) of sulfate pulp, it is necessary to combine oxidative treatment with different reagents in several (from two [106] to five – seven [107]) stages.

Since the 1950s, a large number of publications has appeared that are devoted to the problem of more efficient lignin oxidation with oxygen and hydrogen peroxide aimed at the development of environmentally safe technologies. It should be noted that hydrogen peroxide was used first only for the 'oxygen-induced' type of lignin transformations (quite often together with molecular oxygen [107]) because most of researchers referred to the hydroperoxide anion exclusively as the class of 'lignin-preserving reagents',[10, 75] probably judging from the results of industrial application of these reagents in pulp bleaching.

V. Lignin activation towards oxidative action of oxygen and hydrogen peroxide

Not only chlorine but also nitrogen oxides NO and NO_2 can be used in the bleaching of sulfate pulps.[108] The pulp treated with these oxides is then better bleached with sodium hypochlorite or hydrogen peroxide rather than undergo alkaline extraction as a version of processing.

The use of nitrogen oxides or a system HNO_3-NaNO_2 to increase the efficiency of subsequent sulfate pulp delignification with oxygen has been described.[109–112] The treatment with nitrogen oxides was applied as an 'activating stage'. According to the published data,[111] the effect of activation is based on lignin fragmentation as the result of electrophilic substitution and elimination of side chains in phenol–propane structural units, together with partial destruction of the residual lignin. The electrophilic reagent in this process is NO_2^+ generated in the reaction mixture.[113]



Preliminary activation with nitrogen oxides makes it possible to reduce twofold the content of lignin in pulps (hardness) following treatment with oxygen (or H_2O_2 under conditions of the 'oxygen'[109–112] mechanism): from 10 to 5 Kappa units§ for different sorts of pulps. The minimum value of pulp hardness given in some studies[109–112] equals 3.5 Kappa units, while that in another study was[114] ~ 7.0–7.5 Kappa units. In the latter work, the pulp pretreatment with other oxidants (chlorine, chlorine dioxide, ozone, *etc.*) was proved to be efficient. It has also been found[111] that the selectivity of the sulfate pulp delignification with oxygen and hydrogen peroxide is higher in the case of preliminary pulp treatment with chlorine and ozone than with nitrogen oxides. The minimum hardness of pulps was 6–9 Kappa units after treatment with chlorine (chlorine usage rate was 1%–3% with respect to the mass of absolutely dry pulp) and 6.1 Kappa units after ozonolysis (O_3 usage rate — 1%) at the degree of polymerisation in the range of 1300–1400. This degree of polymerisation without pulp pretreatment was observed only for pulps with hardness of about 15 Kappa units (after pulp delignification with oxygen under pressure of 0.5 MPa in the presence of 0.5% $MgSO_4$ at 110 and 120 °C or with hydrogen peroxide under the same conditions in the presence of 4% NaOH).

It should be noted that a mixture of nitrogen oxides and oxygen was initially proposed to be used in the pulp pretreatment step for lignin activation.[112] However, oxygen only caused stronger destruction of cellulose. Methods involving lignin activation with nitric acid permit removal of up to 75% of residual lignin from pulps.¶

One of extremely toxic side products of the lignin nitration is hydrogen cyanide, which is formed at high concentrations of nitrogen oxides. Sodium nitrite, nitrous acid, peroxynitric acid as well as a redox-composition $NaNO_2-H_2SO_4$ and some others have been proposed as safer reagents.[116, 117] After oxidation in these systems and delignification with oxygen, the content of lignin in pulps is reduced to 8–9 Kappa units.

The common principle of the methods of lignin oxidation considered above (oxidation during bleaching of the sulfate pulp) based on lignin activation by the action of nitrogen oxides, chlorine and chlorine dioxide is as follows: $(E^+ + H_3O^+)-(E^+ + OH^-)$, *i.e.*, an electrophile in an acidic medium – an electrophile in an alkaline medium (see also Refs 118–121).

It has been shown[122–126] that hydroperoxide anions also delignify pulps even somewhat better than oxygen and concomitant radicals generated upon hydrogen peroxide decomposition (or directly upon the action of O_2). In the absence of a hydrogen peroxide stabiliser and at pH ⩾ 12, the realisation of the mechanism $H_2O_2 \rightarrow O_2$ leads to 45% delignification of the sulfate softwood pulp, while in the presence of a stabiliser (sodium silicate, *etc.*) and at pH about 10 solubilisation of the residual lignin reaches 50% at the initial content of lignin of 76 permanganate units (p. u.).[127] However, even this depth of lignin conversion is achieved only in the case of pretreatment of unbleached pulp with a weakly acidic solution for removal of cations of transition metals. Preliminary washing of sulfate pulps with acids or solutions of chelating reagents reduces the loss of hydrogen peroxide due to its decomposition and to some extent decreases pulp destruction with superoxide radical anions.

Methods of acid-catalysed and acid-electrophilic activation of the residual lignin based on acid treatment of the residual lignin in sulfate pulps and aimed at partial hydrolysis of the C(β)–O–C(4) ether bonds at temperatures above 70 °C have been proposed.[123–126, 128–131] Such pretreatment not only changes the structure of the residual lignin, but also activates it to the action of the hydroperoxide anions owing to formation of the carbonyl groups near the site of the ether bond cleavage. Following acid-catalysed activation, the degree of lignin conversion in sulfate hardwood pulps is increased from 0.5 to 0.8 upon the oxidative destruction with hydroperoxide anions. The addition of an oxidant (hydrogen peroxide, monoperoxysulfuric acid)

§ The Kappa unit characterises the lignin content in industrial pulps accepted as a standard unit in Russian State Standard 1 007 074 and in a number of foreign standards.

¶ Quantification of lignin in pulps expressed in Kappa units gives overestimated values for the depth of delignification compared to that determined by photometry.[115]

at the stage of activation leads to additional fragmentation of lignin and its more rapid solubilisation in the next technological step including oxidation with the hydroperoxide anions.

The acid-catalysed activation makes somewhat more efficient the lignin destruction under the action of oxygen in highly basic media. However, this effect is nearly the same as that achieved on treatment of lignin with acids at room temperature (removal of cations and destruction of sulfides [130]) or with chelating reagents [132, 133] where the maximum degree of lignin conversion is about 0.5 and cellulose undergoes higher hydrolytic destruction.

In general, all schemes of oxidative delignification of the type 'reagent + catalysis' can be arranged according to the degree of lignin conversion in sulfate pulps in the following order:[131] oxygen in alkaline media ($O_2 + OH^-$); hydroperoxide anions in alkaline media ($HOO^- + OH^-$); acid-catalysed activation + oxygen in alkaline media [$(H_3O^+)-(O_2 + OH^-)$]; acid-electrophilic activation + oxygen in alkaline media [$(NO_2^+ + H_3O^+)-(O_2 + OH^-)$]; acid-catalysed activation + hydroperoxide anions in alkaline media [$(H_3O^+)-(HOO^- + OH^-)$]; acid-electrophilic activation + hydroperoxide anions in alkaline media [$(OH^+ + H_3O^+)-(HOO^- + OH^-)$].

The selectivity of action of hydroperoxide anions on the residual lignin in sulfate pulps is described by a plot of the degree of cellulose polymerisation as a function of the degree of lignin conversion (Fig. 1).

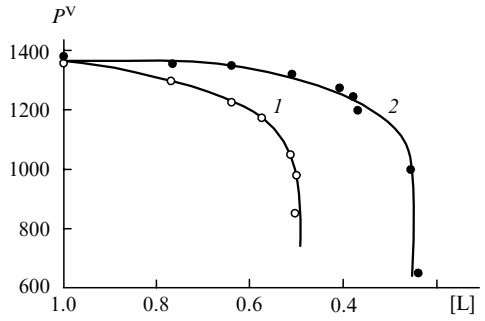


Figure 1. Dependence of the degree of polymerisation (P^v, measured by viscosimetry) on the relative lignin content {[L]} of sulfate softwood cellulose upon delignification under the action of HOO^-: (*1*) without preliminary activation; (*2*) after preliminary acid-catalysed activation.

In the studies on the mechanism of the acid-catalysed activation it was found that the reduction of activated lignin in sulfate pulps with sodium borohydride at pH 10 leads to partial deactivation of lignin [129, 130] towards the hydroperoxide anions. In this particular case, successive treatment of lignin with two different nucleophilic reagents did not give the expected result, although the former ($NaBH_4$) acts as a reducing agent, and the latter (HOO^-) acts as an oxidant.

VI. Ozonolysis of sulfate pulps

Ozonolysis is one of the methods of delignification of sulfate pulps in the course of bleaching. The selectivity of lignin oxidation in the ozonolysis depends on the conditions and, first of all, on the pH of a medium. In neutral media (pure water), destruction of cellulose predominates.[97] To perform the sulfate pulp delignification, ozonolysis is carried out in acid media (pH 2–3) in which, as well as in alkaline media, the destruction of cellulose is substantially lower.[97] The selectivity of delignification is also influenced by the character of the preozonolysis treatment and by the lignin content in pulps subject to ozonolysis.[131]

The products of lignin ozonolysis formed upon treatment of unbleached sulfate softwood pulps with ozone are not dissolved instantly (Figs 2 and 3, curves *1*). Using photometric assay of the lignin content, it was found that the changes in selectivity of the

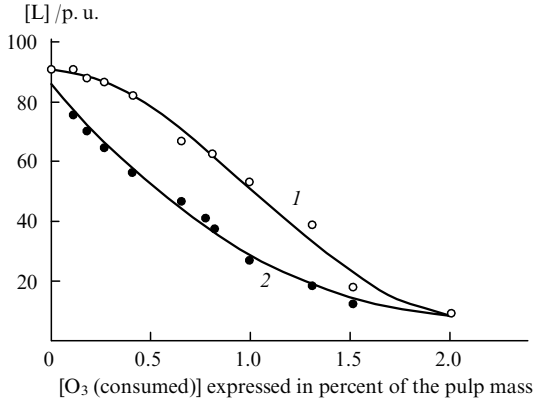


Figure 2. Dynamics of changes in lignin content {[L]} in sulfate softwood pulp during its delignification with ozone: (*1*) ozonolysis; (*2*) ozonolysis and subsequent extraction with a solution of NaOH; p. u. are permanganate units.

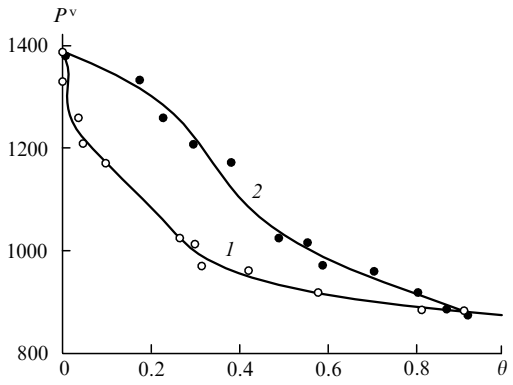


Figure 3. Selectivity of delignification of sulfate softwood pulp with ozone (θ is the degree of lignin conversion equal to the portion of solubilised lignin): (*1*) after ozonolysis; (*2*) after ozonolysis and extraction with a solution of NaOH.

oxidative processes during the ozonolysis of sulfate softwood pulps have a rather unusual character. At high lignin contents in pulps, the destruction of cellulose is predominant. Then, in parallel with a decrease of the lignin content, the direction of the process is gradually changing and, after dissolution of a half of the initial lignin, the selective pulp delignification becomes the major process.† A part of ozonolysed lignin is dissolved in an alkaline medium (Figs 2 and 3, curves *2*). Special tests have shown that destruction of cellulose upon ozonolysis in the presence of lignin is higher indeed. The ozonolysis of pulps partially delignified by other reagents (*i.e.*, semibleached) is also accompanied by destruction of cellulose. However, this destruction is always less than in the ozonolysis of unbleached pulps with high initial lignin content.

The highest degree of the residual lignin oxidation and complete solubilisation of the ozonolysis products in acid media are observed in the case of lignin pretreatment with hydroperoxide anions.[136] A similar effect is achieved on treating lignin with sodium borohydride. Obviously, a decrease in the number of carbonyl and aldehyde groups in the side chains of the lignin phenol–propane units due to their oxidation or reduction (upon the action of HOO^- or BH_4^-, respectively) favours more selective oxidation of lignin aromatic rings with ozone.

The best results are achieved by successive treatment of lignin, at first, with hydrogen peroxide in an acid medium (with

† Assay of lignin content {[L]} by permanganate method [127] (especially in Kappa units [107, 127, 134, 135]) in pulps with a low lignin content typical of semibleached pulps can be incorrect because of deviation of the relationship 'Kappa number–lignin rate' from linearity at [L] $\leqslant$ 1%–2%.

Table 7. Effect of sulfate softwood pulp pretreatment on solubilisation of the residual lignin in the ozonolysis (reagent usage rate constituted 0.225% from the mass of absolutely dry pulp).[131]

Pretreatment scheme	Lignin content prior to ozonolysis [a]	Lignin content after ozonolysis [a]		Degree of delignification in one and two stages (%)		Portion of solubilised lignin (%) [b]
		O_3	O_3 – NaOH	O_3	O_3 – NaOH	
Without pretreatment	91	87	68	4	25	16
OH^+ – HOO^-	33	11	11	67	67	100
OH^+ – ($H_2O_2 \rightarrow O_2$)/NaOH	39	30	23	23	41	56
OH^+ – NaOH	51	38	33	25	35	71
H_3O^+	58	46	41	21	29	72

[a] Expressed in permanganate units. [b] At pH ≈ 2.

peroxyacids), then with a solution of hydrogen peroxide stabilised at pH 10 and finally with ozone in an acid medium ($OH^+ \rightarrow HOO^- \rightarrow O_3$, Table 7).[131]

Thus, according to both absolute and relative parameters, the maximum solubilisation of the residual lignin in the ozonolysis of semibleached sulfate pulps is achieved after pretreatment with hydroperoxide anions. On the whole, with consideration of sulfate pulp cooking and preliminary acid-catalysed electrophilic activation, the optimum sequence of the operations is as follows: sulfate cooking ($SH^- + OH^-$) → acid-catalysed electrophilic activation ($OH^+ + H_3O^+$) → delignification with hydroperoxide anions ($HOO^- + OH^-$) → ozonolysis ($O_3 + H_3O^+$), *i.e.*, an alternation of treatments in acid and alkaline media.

VII. A schematic approach to the selective destruction of residual lignin with peroxy reagents

The oxidative destruction of lignin as a heterochain polymer containing ether bonds predominantly of the C(β)–O–C(4) type occurs under conditions of acid or base catalysis.[12, 13, 137] The alternation of the action of acids (H_3O^+) and bases (OH^-) allows one to achieve partial sulfate pulp delignification.[124] It should be noted, however, that the treatment of pulps according to the HCl–NaOH scheme requires rather drastic conditions and the selectivity of delignification is low: along with twofold reduction of the lignin content, the degree of polymerisation of cellulose is also diminished almost twice.[122] The analysis of the published data on delignification of industrial pulps with chlorine-containing reagents and oxygen in alkaline media as well as the experimental studies of various compositions of oxidising reagents and media have shown that the oxidation schemes without alternation of treatments in acid and alkaline media are less efficient (Table 8).[131]

The properties and reactivities of lignins depend on the methods of their preparation. Therefore, the schemes in Table 8 include the stage of sulfate cooking.

In order to achieve selective oxidative lignin destruction under the action of peroxy reagents with minimal changes in cellulose, it is necessary to apply a complex of different chemical operations which combine a pulp delignification stage and a stage of activation of the residual lignin towards the action of other reagents.

The residual lignin is more labile than cellulose, and its reactivity depends on the method of its preparation or pretreatments. Therefore, enhancement of reactivity of lignin as a result of activation is also a method for an increase in the selectivity of the sulfate pulp delignification.

An electrophilic attack of lignin by peroxy reagents (hydrogen peroxide, peroxy acids, ozone) is realised in acid media, whereas the presence of stabilisers and weakly alkaline media are necessary for treatment of lignin with nucleophiles.[8–10]

On the basis of the aforesaid, the most important factors affecting the selectivity and depth of the sulfate pulp (and other pulps) delignification can be deduced. These are:

(1) the reactive form of a reagent;

(2) the nature and the number of reactive sites in the residual lignin;

(3) acid – base catalysis;

(4) cooking method and type of pulp pretreatment.

As the result of an analysis of the selectivity and depth of oxidative destruction of lignin with different chlorine- and oxygen-containing reagents, a general statement concerning the selectivity of oxidative lignin destruction with peroxy reagents has been formulated:[131] the oxidative destruction of the residual lignin is a maximum provided the stages based on the action of electrophilic and nucleophilic reagents alternate, and that the

Table 8. Schematic presentation and operational schemes for oxidative destruction of residual sulfate lignin.

Schematic presentation	Operational scheme	Catalysis	Degree of lignin conversion (%)	Ref.
$(N^-)-E^+-N^-$	$(Na_2S)-H_2SO_5-H_2O_2$	–	80–83	104, 116
	$(Na_2S)-HCl-H_2O_2$	$(OH)-H_3O^+-OH^-$	70–80	112, 114
	$(Na_2S)-H_2SO_4-H_2O_2$	$(OH)-H_3O^+-OH^-$	70–80	116
	$(Na_2S)-Cl_2-NaOH$	–	70–80	39, 124, 125
$(N^-)-E^+-E^+$	$(Na_2S)-NO_2-O_2$ / NaOH	$(OH^-)-H_3O^+-OH^-$	50–70	98–102, 105, 107–111
	$(Na_2S)-NO_2-H_2O_2$ / NaOH	$(OH^-)-H_3O^+-OH^-$	50–70	98–102, 105, 107–111
$(N^-)-E^+$	$(Na_2S)-O_2$ / NaOH	$(OH^-)-OH^-$	≤50	37, 96, 98, 105
	$(Na_2S)-H_2O_2$ / NaOH	$(OH^-)-OH^-$	≤50	37, 96, 98, 105
$(N^-)-N^-$	$(Na_2S)-H_2O_2$	$(OH^-)-OH^-$	<50	104, 112, 114

Note. Here and in Table 9, the reagents and species participating in the process of sulfate cooking are presented in parentheses; E^+, electrophile, N^-, nucleophile.

most complete destruction of the chromophore-containing structures is achieved by the action of electrophilic reagents in acid media and of nucleophilic reagents in alkaline media as described by the general formula $[(E^+ + H_3O^+) - (N^- + OH^-)]_n$.

At first glance (from the position of organic chemistry), this statement seems to be obvious. However, its formulation became possible only after development of the methods of pulp delignification with hydroperoxide anions, acid-catalysed and acid-electrophilic activation of the residual lignin as well as after studies on ozonolysis of unbleached and semibleached sulfate pulps [114, 124–126, 128–130] and generalisation of studies on activated pulp delignification with oxygen in alkaline media.[109–112, 118–121] All this made it possible to establish a close relationship between the general concepts of organic chemistry and new experimental results obtained in studies on the sulfate pulp delignification with peroxy reagents.

Deviations from the order of operations described above (including the cooking stage) lead to substantial decrease in the lignin reactivity towards oxidants (even to such a reactive one as chlorine dioxide) and, as a consequence, to a decrease in the depth of oxidative delignification and to loss of the pulp brightness (Table 9).

Table 9. The effect of the sequence of oxidative treatments on the depth of delignification of sulfate softwood pulps.

Run	Schematic presentation	Reagents	Degree of lignin conversion (%)	Pulp brightness (%)
1	$(N^-)-E^+-N^-$	$ClO_2-H_2O_2$	91	79
2	$(N^-)-N^--E^+$	$H_2O_2-ClO_2$	85	62
3	$(N^-)-E^+-N^-$	$ClO_2-H_2O_2$	82	80
4	$(N^-)-N^--E^+$	$H_2O_2-ClO_2$	87	65
5	$(N^-)-E^+-N^-$	$H_2O_2-H_2O_2$	52	64
6	$(N^-)-N^--E^+$	$H_2O_2-H_2O_2$	40	57

Note. Usage rates for reagent are the same in pairs of runs: (*1*) and (*2*), (*3*) and (*4*), (*5*) and (*6*). Usage rate: ClO_2 in runs (*1*), (*2*), 0.8%, in runs (*3*), (*4*), 1.3% from the pulp mass; H_2O_2 in runs (*1*)–(*4*), 2.0%, in runs (*5*), (*6*), 1.0% [run (*5*) at pH 2 and 10, run (*6*) at pH 10 and 2 in the first and second stages, respectively].

On the basis of the statement mentioned above, a number of methods for sulfate pulp bleaching and ways of activation of the residual lignin with hydrogen peroxide and ozone have been proposed [124, 125, 129, 130] which are not inferior in the selectivity of delignification to the bleaching processes based on the use of chlorine-containing compounds.

VIII. Kinetic methods for assessment of residual lignin reactivity

Depending on the mechanism of lignin destruction, different kinetic models for assessment of its reactivity are employed. Most often, these are correlations for homogeneous reactions with an assumption that these reactions are homogeneous and heterophasic [138] and that the volume of the phase where the reaction takes place is constant.[139, 140]

In addition to the kinetic methods for examination of homogeneous reactions,[141] kinetic models of topochemical reactions are widely applied for description of chemical transformations of lignin, first of all, the Avraami–Kolmogorov–Erofeev equation.[142] The validity of this equation is substantiated only formally, while no physical correlation between topochemical models and the processes of delignification has been found. It was shown [143] that a diffusion kinetics model is more appropriate to the description of the kinetics of softwood pulp delignification in organic solvents in which the rate-determining step is diffusion of lignin and hemicellulose destruction products into the cooking solution.

Since lignin is a polymer which is chemically and physically bound in pulp to polysaccharides the processes of the lignin chemical transformations should be considered as reactions in a polymeric matrix. The kinetics of chemical reactions in polymers is featured by the influence of various levels of the local matrix organisation and temperature-dependent matrix reorganisations on the conformity to the Arrhenius law, what is manifested in the so-called polychronous kinetics.[144–147]

A model of polychronous kinetics has been used for the fist time by Bel'kova *et al.*[148, 149] in the study of pulp delignification with nitric acid. Later, this model was applied to the study of softwood lignin destruction in alkaline media [150–153] and to oxidative lignin destruction in pulp bleaching processes.[130, 154–156] The application of the polychronous kinetics theory to the description of processes of chemical destruction and solubilisation of lignin (*i.e.*, wood delignification) under the action of various reagents is based on three postulates. The first one is that reactions occur either in a solid phase or in an interface and are characterised by kinetic non-equivalence of chemically homogeneous species. The second one is that under isothermic conditions the processes do not proceed to completion, and at a certain depth of the conversion, the sharp deceleration of the reactions (the so-called kinetic stop) takes place. The third postulate says that the depth of the conversion depends on the temperature.

Thus the major features of chemical processes that follow the polychronous kinetics are their kinetic stop and non-observance of the principle of the temperature–time superposition. Although at higher temperature the reactions proceed deeper, they also stop at a certain point. According to the 'classical' approach,[144]

$$n(\tau, T) = n_0 \int_{\ln k_{\min}}^{\ln k_{\max}} f(\ln k) G(k, \tau) d\ln k = n_0 \int_{\ln k_{\min}}^{\ln k^*} f(\ln k) d\ln k,$$

where $n(\tau, T)$ is the number of species which has entered into the reaction after time τ at temperature T; $f(\ln k)$ is a distribution function; $G(k, \tau)$ is a function describing the kinetics of the process in an elementary group with fixed values of the activation energy (E); $k(E) = k_0 \exp(-E/RT)$ is the reaction rate constant; $k_{\min}$ and $k_{\max}$ are the minimum and maximum rate constants, respectively; G for the simplest case is expressed as $G_1 = \exp(-k_1\tau)$.

The kinetic curves are straightened in the coordinates $C/C_0 - \ln \tau$ (straight lines of the type $y = ax + b$). From these equations the values for $k_{\min}$, $k_{\max}$ and the parameter of the kinetic non-equivalence [$S = \ln(k_{\max}/k_{\min})$] are found using the relationships [144]

$$1 - \theta = a - b \ln \tau,$$

where $a = 1 - \ln 1.76 k_{\max}/\ln(k_{\max}/k_{\min})$, $b = (\ln k_{\max} - \ln k_{\min})^{-1}$. In general case, $\ln \tau = \ln k$.

Recent publications [146, 147] consider the kinetic peculiarities of reactions in a polymeric matrix not as a violation of the classical Arrhenius law but, in contrast, as a particular case of a general model for polychronous kinetics (the so-called integral Arrhenius law).

As a rule, in studies of the delignification processes (including those for oxidative destruction of the residual lignin), the necessity of imposing limitations in the framework of the formal kinetic analysis often arises. Such a lignocellulosic composite as unbleached sulfate pulp is so complex in structure and functional composition that the formulation of a direct kinetic model for the description of its oxidative destruction under the action of radicals and ions generated from peroxy reagents seems to be impossible.

By comparison with other kinetic approaches, the model of polychronous kinetics allows one to characterise more completely the processes of oxidative destruction of the residual lignin by the effects observed in delignification of a lignocellulosic material (see Refs 154–157 on polychronous kinetics for the oxidative deligni-

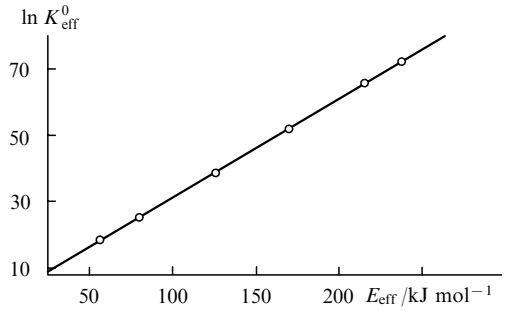


Figure 4. Kinetic compensative effect.

fication of sulfate pulps with hydroperoxide anions and oxygen). The main kinetic peculiarities of oxidative lignin destruction (on bleaching of sulfate softwood pulps) with peroxy reagents include the existence of the kinetic stop and kinetic compensative effect (KCE, a linear relationship between preexponential factors K^0_{eff} for separate ensembles of macromolecules and effective activation energy E_{eff}, Fig. 4), the dependence of the highest degree of lignin conversion (from 0.07 to 0.55 [157]) on the parameter of kinetic non-equivalence S and temperature (Fig. 5) and the non-linear character of the relationship between $\ln\tau$ and $1/T$ in the temperature range from 293 to 373 K (Fig. 6).

The values of the rate constants (k) for oxidative delignification in the temperature interval from 80 to 100 °C range approximately from $10^{17}\exp(-143\text{ kJ mol}^{-1}/RT)\text{ s}^{-1}$ to $16\exp(-19\text{ kJ mol}^{-1}/RT)\text{ s}^{-1}$. The larger values correspond to low-temperature processes with a degree of lignin conversion $\theta = 0.35$, while the smaller values of the rate constant correspond to high-temperature processes with a degree of lignin conversion $\theta = 0.10$.

At a low degree of lignin conversion ($\theta \leqslant 0.1$) under the action of hydroperoxide anions, the rate of delignification is apparently determined by diffusion of the soluble products of lignin destruction (their molecular weight can reach 15 000 – 25 000) from the lignocellulosic matrix.[148] Preliminary treatment of the residual lignin does not virtually affect the rate of the pulp delignification, since this treatment does not change the structure of cellulose fibres. With an increase in the degree of lignin conversion, the rate of the process sharply (exponentially) falls down, while the effective energy of activation rises. These effects are probably caused by slow molecular relaxation in a polymeric matrix so that the time for realisation of the most energetically favourable activated complex during an elementary reaction act (a kinetic constituent) is insufficient.[144]

On the one hand, the acid-catalysed and acid-electrophilic activations of the residual lignin lead to its destruction and better solubilisation (due to the smaller size) in alkaline media. On the other hand, they activate the lignin electrophilic sites. In the range of moderate temperatures (313 – 333 K), the preactivation results

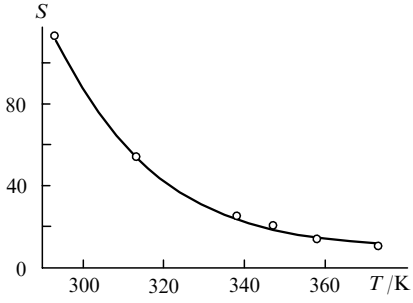


Figure 5. Effect of temperature on the parameter of lignin kinetic non-equivalence (S) in the oxidative pulp delignification with hydrogen peroxide.

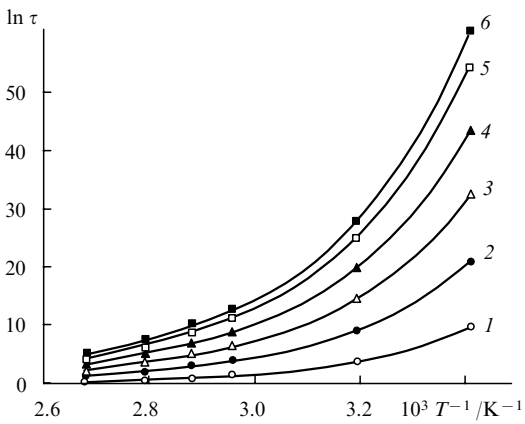


Figure 6. Plot of $\ln\tau$ as a function of $1/T$ for various ensembles of lignin macromolecules in the sulfate pulp delignification in a stabilised solution of hydrogen peroxide at $\theta = 0.1$ (*1*); 0.2 (*2*); 0.3 (*3*); 0.4 (*4*); 0.5 (*5*); 0.55 (*6*).

in diminishing of the kinetic non-equivalence for lignin reactive sites (at 333 K the activated lignin has $S = 21 - 23$, while non-activated one has $S \sim 30$). Despite the fact that the values of the minimum rate constant differ for different methods of lignin preactivation and that this constant bears an obvious physical meaning [$-\ln k_{min} = \ln\tau_{(\theta = 1.00)}$, where $\ln\tau_{(\theta = 1.00)}$ is a logarithm of the time of complete lignin conversion], unambiguous interpretations based on analysis of this constant are hardly possible due to the very low values of this constant. The main manifestation of the lignin activation is an increase in the maximum degree of lignin conversion in its oxidative destruction with hydroperoxide anions and certain decrease in the parameter of kinetic non-equivalence associated probably with destruction-induced changes in the morphological structure of cellulose fibres.

IX. Conclusion

Lignin substantially differs in its behaviour in chemical reactions from low-molecular-weight model compounds, first of all, in a diversity of transformations and their depths. The reactivity of the residual lignin and the depth of its oxidative destruction with peroxy reagents depend to a considerable extent on the character of chemical pretreatments, which functionalise lignin and affect various structural changes in the polymeric lignocellulosic matrix. The depth of lignin destruction in the processes of pulp bleaching with peroxy reagents can be enhanced owing to alternation of the action of electrophilic and nucleophilic reagents under conditions of acid and base catalysis, respectively.

However, the quantitative assessment of the lignin reactivity is rather difficult to perform because of the chemical and structural (topological and supramolecular) heterogeneity of industrial lignin, structural heterogeneity of the polymeric lignocellulosic matrix and some kinetic peculiarities of reactions in polymers. Aforementioned features of lignin, its polyfunctionality as well as diversity of oxidants, generated in reactions of oxygen, hydrogen peroxide and ozone, and the differences in mechanisms of the reactions of these reagents with lignin in acid and alkaline media provide a reason to consider the oxidative destruction of the residual lignin as a complex fundamental problem that demands further investigations.

Despite some achievements in the studies of lignin reactions, an increase in the reactivity of the residual lignin remains a very important practical problem due to the permanently rising requirements for the environmental safety of technological processes in the pulp industry. Examination of the behaviour of lignin in chemical reactions and technological processes involving hydrogen peroxide, oxygen and ozone is not unambiguous, and further investigations and data systematisation are necessary in this field. Exploration of selective oxidative lignin destruction is a

very important direction in wood chemistry, organic chemistry, chemistry of high-molecular-weight compounds and related fields of the sciences.

References

1. B D Bogomolov *Khimiya Drevesiny i Osnovy Khimii Vysokomolekulyarnykh Soedinenii* (The Chemistry of Wood and Foundations of the Chemistry of High-Molecular Compounds) (Moscow: Lesnaya Promst, 1973)
2. V Yu Belyaev, Candidate Thesis in Chemical Sciences, Institute of Chemistry, Komi Scientific Centre of Ural Branch, Russian Academy of Sciences, Syktyvkar, 1998
3. J B Monakov, V Yu Belyaev, A P Karmanov, T V Moskvicheva *Dokl. Akad. Nauk* **333** 200 (1993) [a]
4. J S Gratzl *Das Papier* **41** 120 (1987)
5. Ya A Gravitis, Doctoral Thesis in Chemical Sciences, Institute of Chemistry of Wood, Riga, 1989
6. A P Karmanov, Doctoral Thesis in Chemical Sciences, Institute of Chemistry, Komi Scientific Centre of Ural Branch, Russian Academy of Sciences, Syktyvkar, 1995
7. P P Erin'sh, I F Kul'kevitsa *Khim. Drev.* (6) 61 (1990)
8. J Gierer *Holzforschung* **36** 55 (1982)
9. J Gierer *Holzforschung* **44** 387 (1990)
10. J Gierer *Holzforschung* **44** 395 (1990)
11. J P Simon, K-E L Eriksson *Holzforschung* **49** 429 (1995)
12. K Sarkanen, K Lyudvig (Ed.) *Ligniny (Struktura, Ssvoistva i Reaktsii)* [Lignins (Structure, Properties and Reactions)] (Moscow: Lesnaya Promst, 1975)
13. V M Nikitin, A V Obolenskaya, V P Shchegolev *Khimiya Drevesiny i Tsellyulozy* (The Chemistry of Wood and Cellulose) (Moscow: Lesnaya Promst, 1978)
14. J F D Dean, K-E L Eriksson *Holzforschung* **46** 135 (1992)
15. D Fengel, G Wegener *Wood: Chemistry, Ultrastructure, Reactions* (Berlin: Walter de Gruyter, 1983)
16. H H Nimz, A Berg, C Granzow, R Casten *Zolz-Zentralblatt* **95/96** 1360 (1988)
17. D H Page *J. Pulp Paper Sci.* **9** 15 (1983)
18. S M Shevchenko, Doctoral Thesis in Chemical Sciences, Wood Technology Academy, St.-Petersburg, 1992
19. K Poppius, Hortling Bo, I Sundquist, in *International Symposium on Wood and Pulping Chemistry (Abstracts of Reports), Atlanta, 1989* p. 145
20. H Nimz, I Mogharab, H D Luedemann *Makromol. Chem.* **175** 2563 (1974)
21. Y Tsutsumi, R Kondo, K Sakai, H Imamura *Holzforschung* **49** 423 (1995)
22. E I Evstigneev, A V Kurzin, Yu A Platonov, E D Maiorova *Zh. Prikl. Khim.* **69** 148 (1996) [b]
23. G Gellerstedt, E-L Lindfors, in *Proceedings of the International Pulp Bleaching Conference, Stockholm, 1991* Vol. 2, p. 73
24. A P Karmanov, J B Monakov *Vysokomol. Soedin., Ser. B* **38** 1631 (1996) [c]
25. A P Karmanov, J B Monakov *Vysokomol. Soedin., Ser. B* **37** 328 (1995) [c]
26. P P Erin'sh *Khim. Drev.* (1) 8 (1977)
27. D C Smith, W G Glasser, H R Glasser, T C Ward *Cellul. Chem. Technol.* **22** 171 (1988)
28. K Freudenberg, A S Neish *Constitution and Biosynthesis of Lignin* (Berlin: Springer, 1968)
29. M Matsukura, A Sakakibara *J. Jpn. Wood Res. Soc.* **1** 35 (1969)
30. Ya A Gravitis, V G Ozol'-Kalnin *Khim. Drev.* (3) 24 (1977)
31. Y-Z Lai, K V Sarkanen *Tappi J.* **51** 449 (1968)
32. Y-Z Lai, K V Sarkanen *Cellul. Chem. Technol* **9** 239 (1975)
33. Y-Z Lai, X-P Guo, W Situ *J. Wood Chem. Technol.* **10** 365 (1990)
34. T Yasuda, A Sakakibara *Holzforschung* **35** 1831 (1981)
35. L V Kanitskaya, I P Deineko, D F Kushnarev, A V Klemper, G A Kalabin *Khim. Drev.* (6) 17 (1989)
36. G J Leary, J A Lloyd, K R Morgan *Holzforschung* **42** 199 (1988)
37. E Adler *Wood Sci. Technol.* **11** 169 (1977)
38. A Sakakibara *Wood Sci. Technol.* **14** 89 (1980)
39. W G Glasser, H R Glasser *Pap. Puu* **63** 71 (1981)
40. M Erickson, S Larsson, G E Miksche *Acta Chem. Scand., Ser. C* **27** 903 (1973)
41. H Nimz *Angew. Chem., Int. Ed. Engl.* **13** 313 (1974)
42. J Gierer *Sven. Papperstidn.* **73** 571 (1970)
43. J Gierer, N-O Nilvebrant *Holzforschung (Suppl.)* **40** 107 **(**1986)
44. L A Milovidova, G V Komarova, G A Ivanova, L A Smirnova *Izv. Vyssh. Uchebn. Zaved., Lesn. Zh.* (5–6) 122 (1993)
45. V V Sokolov, D A Sukhov, A V Fedorov *Tsellyul. Bum. Karton* (9–10) 22 (1996)
46. V Martin, K Burneson, H Lee, M Hewitt *Holzforschung* **49** 453 (1995)
47. Yu A Malkov, N I Egorova, V A Zhalina, N M Tarannikov *Tsellyul. Bum. Karton* (11–12) 10 (1997)
48. V A Demin, V D Davydov, B D Bogomolov *Elektrokhimicheskaya Otbelka Sul'fatnoi Tsellyulozy* (Electrochemical Bleaching of Sulfate Cellulose) (Leningrad: Nauka, 1982)
49. E B Althouse, J H Bortwick, D K Jain *Tappi J.* **70** 113 (1987)
50. T A Tumanova *Fiziko-Khimicheskie Osnovy Otbelki Tsellyulozy* (Physicochemical Foundations of Whitening of Cellulose) (Moscow: Lesnaya Promst, 1984) p. 215
51. A Singh *J. Pulp Paper Sci.* **2** 48 (1990)
52. T Elder *Holzforschung* **52** 371 (1998)
53. J H Conkey *Tappi J.* **64** 101 (1981)
54. J L Minor, E L Springer, in *International Symposium on Wood and Pulping Chemistry (Abstracts of Reports), Atlanta, 1989* p.133
55. E N Medvedeva, V V Vershal', V A Babkin *Khim. Interes. Ustoichiv. Razvitiya* **4** 343 (1996) [d]
56. T I Makovskaya, E N Medvedeva, A N Zakazov, F M Gizetdinov, V A Babkin *Izv. Vyssh. Uchebn. Zaved., Lesn. Zh.* (2–3) 96 (1993)
57. D Lachenal, C De Choudens *Cellul. Chem. Technol.* **20** 553 (1986)
58. J Gierer, N-O Nilvebrant *Holzforschung (Suppl.)* **48** 51 (1994)
59. D Lachenal, C De Choudens, L Bourson *Tappi J.* **69** 90 (1986)
60. J Colom, B Roncero, in *The Fifth European Workshop on Lignocellulosics and Pulp. ELWP'98, University of Aveiro, Aveiro, 1998* p. 509
61. C Chirat, D Lachenal *Holzforschung (Suppl.)* **48** 133 (1994)
62. C-A Lindholm *Pap. Puu* **72** 254 (1990)
63. V A Solov'ev, G A Pazukhina *PAP-FOR 93 (Pulp and Paper Forum), St.-Petersburg, 1993* p. 173
64. S A Medvedeva I V Volchatova, V A Babkin *Khim. Interes. Ustoichiv. Razvitiya* **4** 321 (1996) [d]
65. V J J Martin, B K Burnison, H Lee, L M Hewitt *Holzforschung* **49** 453 (1995)
66. T J Smith, R H Wearne, A F A Wallis *Holzforschung* **49** 279 (1995)
67. T Norris, I Luke *Pulp Paper J.* **41** 16 (1988)
68. R J Crawford, M N Stryker, S W Jett, W L Carpenter, R P Fisher, A K Jain *Tappi J.* **70** 123 (1987)
69. V M Reznikov *Khim. Drev.* (2) 3 (1991)
70. E I Evstigneev, E I Chupka *Khim. Drev.* (5) 27 (1990)
71. J Gierer, E Yang, T Reitberger *Holzforschung* **48** 405 (1994)
72. A D Sergeev, E I Chupka *Khim. Drev.* (1) 90 (1983)
73. A D Sergeev, E I Chupka *Khim. Drev.* (2) 73 (1985)
74. A Ya Sychev, V G Isak *Usp. Khim.* **64** 1183 (1995) [*Russ. Chem. Rev.* **64** 1105 (1995)]
75. D Lachenal, L Bourson *Tappi J.* **63** 119 (1980)
76. C W Dence, S Omori *Tappi J.* **69** 120 (1986)
77. E I Chupka, S I Zhirnova, A D Sergeev *Khim. Drev.* (1) 83 (1988)
78. E I Chupka, M E Kondakova, I M Luzhanskaya, S V Egorova, S M Trofimova, V V Fomina, N A Ivanov *Khim. Drev.* (2) 29 (1981)
79. A I Nonni, C W Dence *Holzforschung* **42** 37 (1988)
80. G Gellerstedt, B Pattersson *Sven. Papperstidn.* **83** 314 (1980)
81. G Gellerstedt, E-L Lindfors *Tappi J.* **70** 120 (1987)
82. D D Jones, D C Johnson *J. Org. Chem.* **32** 1402 (1967)
83. A Enoki, M N Gold *Arch. Microbiol.* **132** 123 (1982)
84. R T Morrison, R N Boyd *Organic Chemistry* (Boston: Allyn and Bacon, 1971)
85. J Gierer, F Imsgard, in *International Symposium on Chemistry of Delignification with Oxygen, Ozone and Peroxides (Abstracts of Reports), Tokyo, 1980* p. 133
86. M A Zil'bergleit, T V Korneichuk, V M Reznikov *Khim. Drev.* (6) 21 (1987)
87. M A Zil'bergleit, B S Simkhovich, V M Reznikov *Khim. Drev.* (6) 28 (1987)

88. M A Zil'bergleit, T V Korneichuk, V M Reznikov *Khim. Drev.* (2) 56 (1988)
89. S D Razumovskii *Kislorod — Elementarnye Formy i Svoistva* (Oxygen — Elementary Forms and Properties) (Moscow: Khimiya, 1979)
90. S D Razumovskii, G E Zaikov *Usp. Khim.* **49** 2344 (1980) [*Russ. Chem. Rev.* **49** 1163 (1980)]
91. H S Kaneko, S Hosoya K Iiyama, J Nakano *J. Wood Chem. Techol.* **3** 399 (1983)
92. Y Matsumoto, A Ishizu, J Nakano *Holzforschung (Suppl.)* **40** 81 (1986)
93. S C Puri, S M Anand *Cellul. Chem. Technol.* **20** 535 (1986)
94. H Taneda, N Habu, J Nakano *Holzforschung* **43** 187 (1989)
95. D Bjorn, P Walter *Pap. Puu* **74** 720 (1992)
96. P W-C Ku, J S Hsieh, D M Jaywant, L L Houle *Tappi J.* **75** 146 (1992)
97. V A Demin, N N Kabal'nova, G Ya Osipova, V V Shereshovets *Zh. Prikl. Khim.* **66** 2562 (1993) [b]
98. G G Galiaskarova, Candidate Thesis in Chemical Sciences, Institute of Organic Chemistry, Ural Scientific Centre, Russian Academy of Sciences, Ufa, 1997
99. C Brage, T Eriksson, J Gierer *Holzforschung* **45** 23 (1991)
100. C Brage, T Eriksson, J Gierer *Holzforschung* **45** 147 (1991)
101. C Brage, T Eriksson, J Gierer *Holzforschung* **49** 127 (1995)
102. J Gierer *J. Wood Chem. Technol.* **12**. 367 (1992)
103. V A Demin, A G Dontsov, E V German, T P Shcherbakova, E A Fel'de, in *Lesokhimiya i Organicheskii Sintez* (Wood Chemistry and Organic Synthesis) (Syktyvkar: Komi Scientific Centre, Ural Branch, Russian Academy of Sciences, 1996) p. 71
104. N Liebergott, B Van Lierop *Pulp Paper Can.* **87** 58 (1986)
105. S M Shevchenko, A G Apushkinskii *Usp. Khim.* **61** 195 (1992) [*Russ. Chem. Rev.* **61** 105 (1992)]
106. V A Demin, E I Fedorova, L A Nikulina, E V German, N F Pestova, T P Shcherbakova *Otbelka Sul'fatnoi Tsellyulozy bez Molekulyarnogo Khlora* (Bleaching of Sulfate Cellulose without Molecular Chlorine) (Syktyvkar: Komi Scientific Centre, Ural Branch, Russian Academy of Sciences, 1995)
107. H Sixta, L Lotzingen, A Schrittwieser, P Hendel *Papier* **45** 610 (1991)
108. D Rasmusson, O Samuelsen *Holzforschung (Suppl.)* **40** 147 **(**1986)
109. L Andersson, O Samuelson, P Mansson *Sven. Papperstidn.* **87** 59 (1984)
110. L Andersson, O Samuelson *Sven. Papperstidn.* **88** 102 (1984)
111. D Lachenal, L Bourson, M Muguet, A Chauvet *Cellul. Chem. Technol.* **24** 593 (1990)
112. U Carlson, O Samuelson *Holzforschung* **39** 41 (1985)
113. N N Shorygina, V M Reznikov, V V Elkin *Reaktsionnaya Sposobnost' Lignina* (Reactivity of Lignin) (Moscow: Nauka, 1976)
114. V A Demin *Khim. Drev.* (3) 29 (1994)
115. G Fossum, A Marklund *Tappi J.* **71** 79 (1988)
116. A F Gogotov, Yu V Panasenkov, I L Panchukov, E V Shilkin, V A Babkin *Khim. Interes. Ustoichiv. Razvitiya* **4** 245 (1996) [d]
117. A F Gogotov, Doctoral Thesis in Chemical Sciences, Siberian State Technological University, Krasnoyarsk, 1998
118. P Larsson, O Samuelson, U Ojteg *Holzforschung* **43** 121 (1989)
119. R Larsson, O Samuelson *J. Wood Chem. Technol.* **10** 311 (1990)
120. D Rasmusson, O Samuelson *Cellul. Chem. Technol.* **23** 285 (1988)
121. O Samuelson, U Ojteg *Tappi J.* **71** 175 (1988)
122. Yu A Bobrov, M I Cherezova, V A Demin, in *Khimiya i Tekhnologiya Proizvodstva Tsellyulozy* (The Chemistry and Technology of Production of Cellulose) (Leningrad: Leningrad Technological Academy, 1987) p. 48
123. V A Demin, A P Karmanov, Yu A Bobrov *Khimicheskaya Pererabotka Drevesiny i Drevesnykh Otkhodov* (Chemical Processing of Wood and Wood Waste) (Leningrad: Leningrad Technological Academy, 1988) p. 91
124. Russ. P. 1 193 192; *Byull. Izobret.* (43) 112 (1985)
125. Russ. P. 2 061 134; *Byull. Izobret.* (15) 244 (1996)
126. Russ. P. 2 019 612; *Byull. Izobret.* (17) 98 (1994)
127. A V Obolenskaya, V P Shchegolev, G L Akim, E L Akim, N L Kossovich, I Z Emel'yanova *Prakticheskie Raboty po Khimii Drevesiny i Tsellyulozy* (Practical Works on Chemistry of Wood and Cellulose) (Moscow: Lesnaya Promst, 1965)
128. Russ. P. 2 019 613; *Byull. Izobret.* (17) 98 (1994)
129. Russ. P. 2 075 566; *Byull. Izobret.* (8) 190 (1997)
130. V A Demin, E V German *Khim. Drev.* (3) 38 (1994)
131. V A Demin, Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, Ural Scientific Centre, Russian Academy of Sciences, Ufa, 1997
132. L A Milovidova, G V Komarova *Tsellyul. Bum. Karton* (11 – 12) 14 (1997)
133. A D Sergeev, V A Petrenev, O P At'man *Tsellyul. Bum. Karton* (5 – 6) 5 (1998)
134. R A D Mbachu, R St J Manley *J. Polym. Sci., Polym. Chem. Ed.* **19** 2053 (1981)
135. H-J Mielisch, J Odermatt, O Kordachia, R Patt *Holzforschung* **49** 445 (1995)
136. A G Dontsov, V A Demin, in *Lesokhimiya i Organicheskii Sintez* (Wood Chemistry and Organic Synthesis) (Syktyvkar: Komi Scientific Centre, Ural Branch, Russian Academy of Sciences, 1996) p. 75
137. Y-Z Lai, S-P Mun *Holzforschung* **48** 203 (1994)
138. M A Zil'bergleit, V M Reznikov *Khim. Drev.* (6) 62 (1988)
139. M A Kushner, L G Matusevich, I V Sen'ko, L V Chirich *Khim. Drev.* (3) 50 (1990)
140. E M Ben'ko, V V Kovaleva, A N Mitrofanova, V A Voblikova, A N Pryakhin, V V Lunin *Zh. Fiz. Khim.* **68** 1580 (1994) [e]
141. E T Denisov *Kinetika Gomogennykh Khimicheskikh Reaktsii* (Kinetics of Homogeneous Chemical Reactions) (Moscow: Vysshaya Shkola, 1988)
142. P Barret *Kinétique Hétérogéné* (Paris: Jauthier-Villars, 1973)
143. G B Tibermane, L T Purina, M Ya Ioelovich, A P Treimanis *Khim. Drev.* (4 – 5) 36 (1992)
144. N M Emanuel', A L Buchachenko *Khimicheskaya Fizika Molekulyarnogo Razrusheniya i Stabilizatsii Polimerov* (Chemical Physics of Molecular Destruction and Stabilisation of Polymers) (Moscow: Nauka, 1988)
145. O N Karpukhin *Usp. Khim.* **47** 1119 (1978) [*Russ. Chem. Rev.* **47** 587 (1978)]
146. V A Kutyrkin *Khim. Fiz.* **14** (5) 71 (1995) [f]
147. V A Kutyrkin *Khim. Fiz.* **14** (5) 90 (1995) [f]
148. L P Bel'kova, V S Gromov, A I Mikhailov *Khim. Drev.* (6) 50 (1980)
149. L P Bel'kova, V S Gromov, A I Mikhailov *Khim. Drev.* (6) 59 (1980)
150. V V Vershal', E I Chupka, O V Ushakovskii, A I Mikhailov *Khim. Drev.* (6) 47 (1988)
151. R Z Pen, I L Shapiro, V R Pen *Khim. Drev.* (3) 33 (1990)
152. R Z Pen, I L Shapiro, V R Pen *Khim. Drev.* (5) 106 (1990)
153. R Z Pen, V R Pen, I L Shapiro, M Yu Katrukhina *Khim. Drev.* (4 – 5) 31 (1992)
154. A P Karmanov, V A Demin *Khim. Interes. Ustoichiv. Razvitiya* **4** 289 (1996) [d]
155. A I Mikhailov, V A Demin, L D Kaplun, G A Kolpakov, I A Shilova, in *The Fifth European Workshop on Lignocellulosics and Pulp. ELWP'98, University of Aveiro, Aveiro, 1998* p. 79
156. V A Demin, A P Karmanov, L S Kocheva, in *The Fifth European Workshop on Lignocellulosics and Pulp. ELWP'98, University of Aveiro, Aveiro, 1998* p. 141
157. V A Demin, E V German-Udoratina, T P Sherbakova, in *The Fifth European Workshop on Lignocellulosics and Pulp. ELWP'98, University of Aveiro, Aveiro, 1998* p. 137

[a] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[b] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[c] — *Polym. Sci. (Engl. Transl.)*
[d] — *Chem. Sustain. Devel. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Russ. J. Chem. Phys. (Engl. Transl.)*