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CATALYTIC REACTION MECHANISMS

New Mechanism for the Catalytic Oxidation of Lignin to Vanillin

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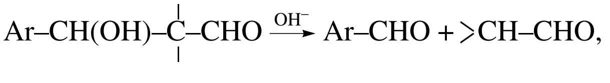
Abstract—The previously proposed mechanism for lignin oxidation to vanillin was supported experimentally. This process begins with the formation of a phenoxyl radical and ends with the step of retroaldol cleavage of substituted coniferaldehyde to vanillin. The oxidation of model compounds was studied, and experimental evidence for the proposed mechanism was obtained. The postulated intermediate coniferyl alcohol was detected in the oxidation of eugenol. The proposed mechanism was supported by kinetic data and the composition of the oxidation products of vanillideneacetone, lignosulfonates, eugenol, isoeugenol, guaiacylethanol, and guaiacylpropanol.

INTRODUCTION

The oxidation of lignins (the main polymer component of wood) to vanillin is among the variety of chemical processes used for the conversion of wood and other renewable plant resources into the products of conventional organic synthesis. On the one hand, this process was implemented on an industrial scale in the 1930s–1940s [1, 2]. On the other hand, even the well-known regularities cannot be explained based on a great number of published hypotheses on the mechanism of oxidative cleavage of the phenylpropane units of lignin to aromatic aldehydes.

The polymeric structure of lignin consists of phenylpropane units containing phenolic hydroxyl. According to the first hypothesis on the mechanism of vanillin formation [3], in the course of the alkaline hydrolysis of lignosulfonates without oxidizing agents, vanillin is formed by the retroaldol cleavage of the α-hydroxy-γ-carbonyl structure of the phenylpropane unit of lignin



$$\mathrm{Ar{-}CH(OH){-}\overset{|}{\underset{|}{C}}{-}CHO} \xrightarrow{OH^-} \mathrm{Ar{-}CHO} + \mathrm{{>}CH{-}CHO}, \quad \text{(I)}$$

where Ar is the 3-methoxy-4-phenoxy anion. The above reaction scheme adequately describes the alkaline hydrolysis of lignin to vanillin in the absence of oxidizing agents. It explains the formation of corresponding aceto derivatives (acetovanillone and acetosyringone) as the by-products of the alkaline hydrolysis of lignins by the analogous process of hydrolysis of an α-carbonyl structure [3, 4]

$$\mathrm{Ar{-}C(O){-}CH_2CR_2OH = Ar{-}C(O)CH_3 + R_2CO}. \quad \text{(II)}$$

Reactions (I) and (II) require a strongly alkaline medium, which is necessary for the formation of a doubly charged enolate anion in the course of aldol condensation and cleavage [5]. Therefore, they can effectively occur only in media that are much more alkaline than that required for the acid dissociation of the phenol groups of lignin (p$K \approx 10$).

The maximum yields of vanillin in the processes of alkaline hydrolysis are 5–6 wt % on a lignin basis [2, 4]. Under the action of the most effective oxidizing agents (nitrobenzene and copper(II)), the yields of aromatic aldehydes increase by a factor of 5–10, and they can be higher than 40–50 mol % [6, 7]. Oxidation with oxygen also increases the yield of hydroxy aldehydes both in the presence and in the absence of catalysts [4, 8]. In almost all cases, the formation of aldehydes was accompanied by the appearance of corresponding aceto derivatives as impurities [4, 6, 8]. High yields of vanillin in oxidation processes are possible only in alkaline media [1–4, 9, 10].

The above facts suggest that the selective formation of vanillin and syringaldehyde from lignin in alkaline media occurs by mechanisms having common features, primarily, the step of retroaldol cleavage, regardless of the nature of the oxidizing agent. Nevertheless, until very recently no attempt was made to use retroaldol cleavage reactions (**I**) and (**II**) as the final step in an analysis of oxidation mechanisms.

The following oxidation mechanism, which involves quinonemethide intermediates **III** and **IIIa** and dioxethane **V** as key intermediates, was proposed [11–13]:

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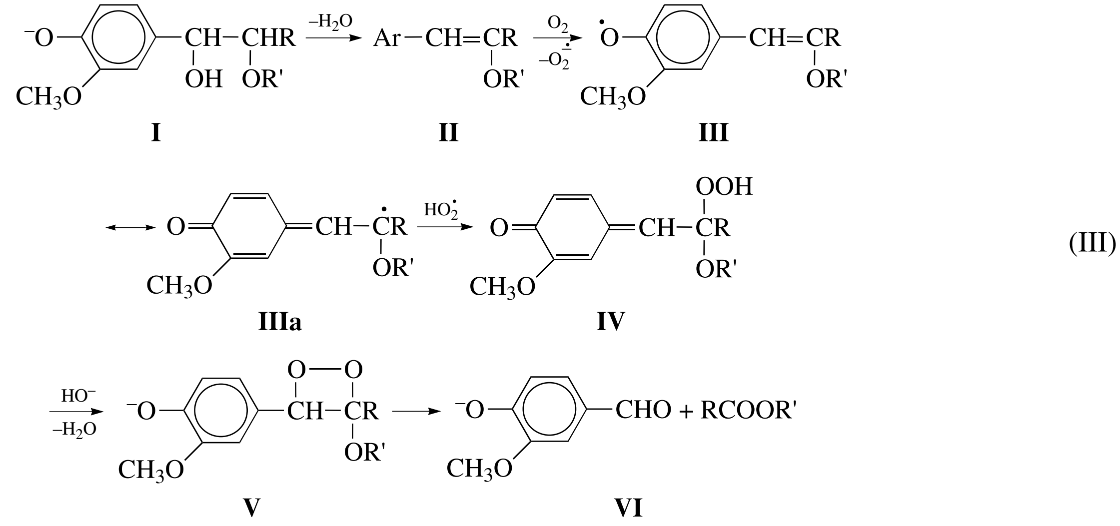
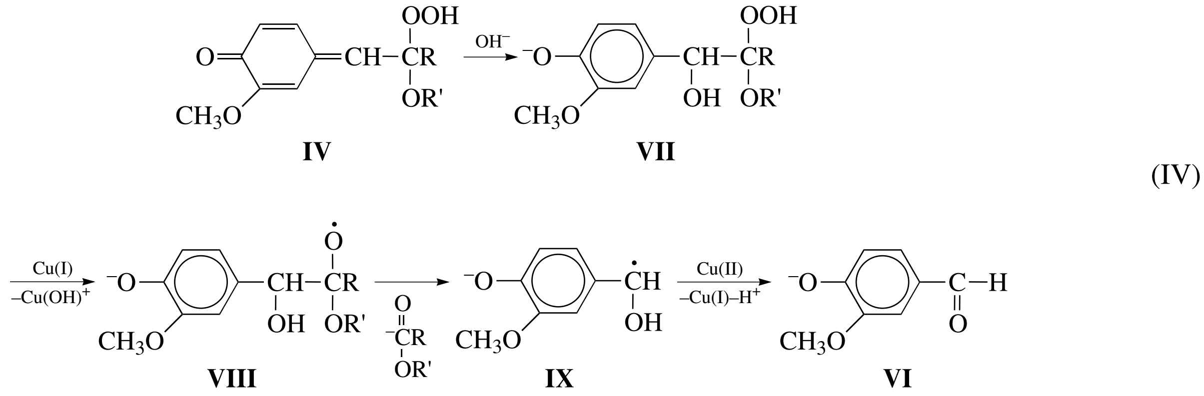


According to [11–13], dioxethane **V** degrades by the synchronous cleavage of C–C and C–O bonds to form vanillate ion **VI**. However, in terms of the mechanism of vanillin formation (reaction scheme (III)), the role of a catalyst is restricted by the acceleration of the step of oxidation of substrate **II** with oxygen, and this cannot explain the well-known fact of an increase in the process selectivity under the action of a catalyst. Moreover, reaction scheme (III), as well as the majority of the hypotheses under consideration, cannot explain the formation of aceto derivatives as by-products.

The following reaction scheme was proposed [9, 14], which combines the formation of quinonemethide hydroperoxide **IV** and the well-known steps of catalytic hydroperoxide decomposition:

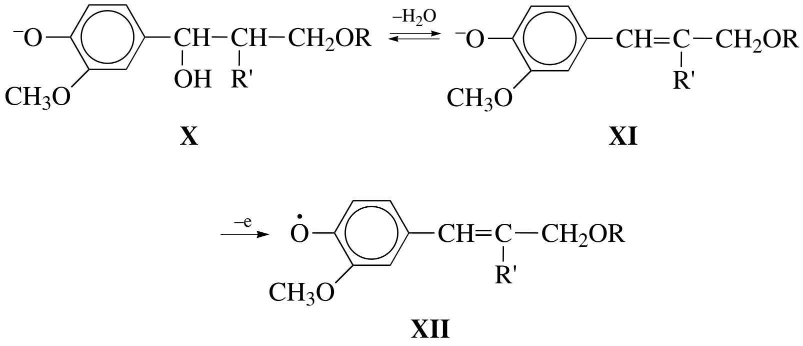


Reaction scheme (IV) explains the effect of a catalyst on the selectivity of the process; however, it does not explain the formation of aceto derivatives as impurities and the necessity of a strongly alkaline medium. According to reaction scheme (IV), oxidation at low pH values gives the dimerization products of radical ion **IX** like dehydrodivanillin; however, these products were not detected experimentally [15].

According to Schultz and Templeton [16], the oxidation of lignin to vanillin begins with electron detachment from hydroxyl at the benzyl group of the phenylpropane unit rather than with electron transfer from the phenolic oxygen of the phenolate anion to the oxidant molecule. This assumption differs fundamentally from the predominant concepts of the occurrence of processes of this type through the formation of phenoxyl intermediates; it is also unsupported experimentally.

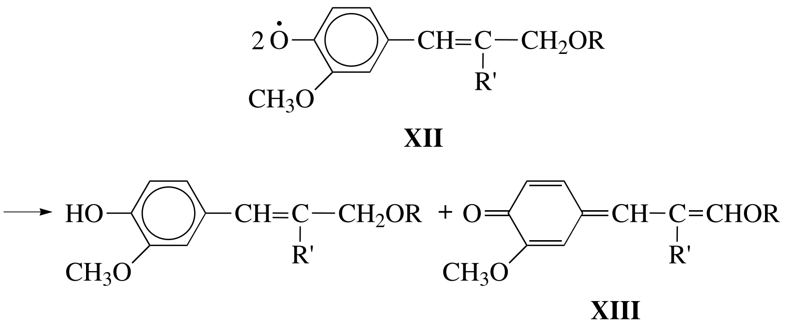
The above survey of the currently available hypotheses on the mechanism of oxidative cleavage of lignins to aromatic aldehydes demonstrates their common disadvantages: they do not explain the necessity of strongly alkaline media for performing the process and the fact that aceto derivatives are formed as by-products.

The mechanism that solves these problems was proposed previously [17, 18]. The oxidation of lignin begins with electron detachment from phenoxy anion **XI**:



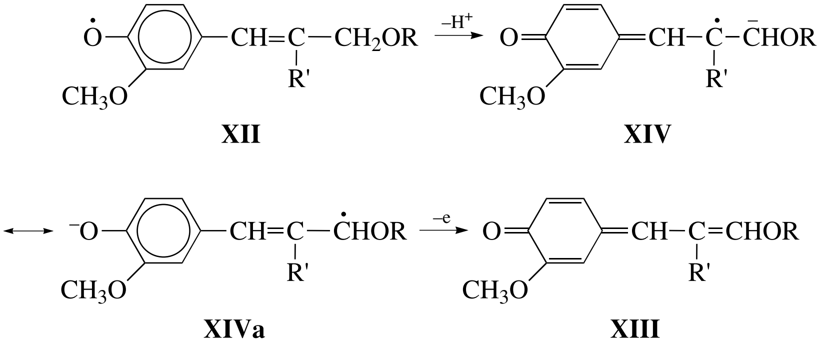
(V)

Resulting phenoxyl radical **XII** is further converted into quinonemethide **XIII**, and this process can occur via several reaction paths: by the disproportionation of the phenoxyl radical [19]



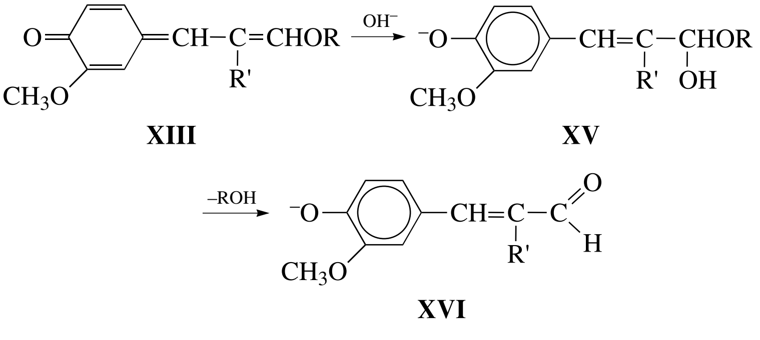
(VI)

or by the oxidation of this radical preceded by proton detachment [17]



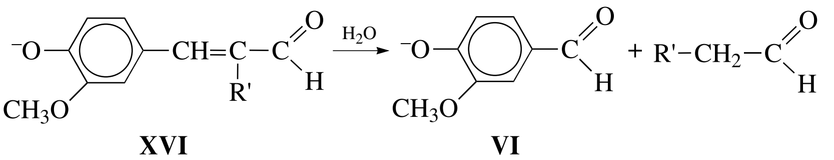
(VII)

The nucleophilic addition of the hydroxide ion to quinonemethide **XIII** forms the structure of coniferaldehyde **XVI**:



(VIII)

The retroaldol cleavage of this aldehyde gives vanillin **VI**:



(IX)

The proposed mechanism explains the formation of aceto derivatives as impurities by the addition of the hydroxy anion at the α-position of quinonemethide **XIII** followed by the retroaldol cleavage of the α-carboxyethylene structure. It is well known that under conditions of thermodynamic control the addition of nucleophiles to quinonemethides occurs at the γ-position, and this can explain the nature of the main product (vanillin, thermodynamic control) and the by-product (acetovanillone) [19].

The mechanism under consideration differs from other hypotheses in the participation of the γ-methyl group of a propane chain in the formation of vanillin, and this difference should manifest itself in the oxidation of guaiacylpropane and guaiacylethane derivatives. Indeed, the vanillin : acetovanillone ratio in the oxidation of guaiacylpropanol was higher than that in the oxidation of guaiacylethanol or ferulic acid by one order of magnitude [17]. This significant difference in the behaviors of structurally similar substrates in the course of alkaline oxidation demonstrates that the γ-carbon atom of the phenylpropane unit plays a key role in the cleavage of the bond between α- and β-carbon atoms. Therefore, this difference provides support for the proposed mechanism (reaction schemes (V)–(IX)) and serves as an argument against the hypotheses considered above.

The aim of this work was to provide additional experimental support for the proposed oxidation mechanism (reaction schemes (V)–(IX)) [17, 18].

EXPERIMENTAL

Fermented alkaline liquor with a dry solids content of 42.6 wt % from the Syas'skii Pulp-and-Paper Mill (Leningrad oblast) was obtained from fir wood by sulfite pulping with the addition of NaOH. The dry solids of the spent sufite liquor contained 18.3% ash, 5.26% hydrogen, 40.5% carbon, 6.05% sulfur, and 65% lignin.

Eugenol with purity higher than 98% from AO Aromasintez (Kaluga) was used in this study. Vanillideneacetone was prepared by the crotonization of vanillin and acetone in an alkaline medium.

The oxidation of lignosulfonates and model compounds was carried out in a rocking stainless steel reactor at 160°C and an argon or oxygen partial pressure of 0.3 MPa. Oxygen, as it was absorbed, was supplied to the reactor from a calibrated buffer vessel using a special valve as described elsewhere [9]. The concentrations of test substances were determined by GLC after the acidification and extraction of samples. Copper hydroxide (10 g/l) was used as a catalyst in the oxidation of vanillideneacetone and lignosulfonates.

To detect the EPR spectra of intermediates, the oxidation of eugenol (1 M) with potassium permanganate (0.05 M) in an alkaline medium (an excess of 1 M NaOH) was performed at room temperature. Manganese(VII) and Mn(VI) do not give EPR spectra; for this reason, permanganate was used in this study. The contact time of working solutions in a mixer was ~0.02 s. A jet from the mixer was directed to a silver plate cooled in liquid nitrogen. The sample was stored in liquid nitrogen. The EPR spectra were measured on an RE-1307 radio spectrometer ($\lambda = 3$ cm) at 77 K.

The resulting spectra were deconvolved into two Gaussian bands:

$$I = \text{const}(\exp(-b(H-a/2)^2) + \exp(-b(H+a/2)^2)),$$

where H is the magnetic field intensity, Oe; I is the EPR signal intensity; a is the hyperfine coupling constant; const and b are constants.

RESULTS AND DISCUSSION

Effect of the alkalinity of solution on the yield of vanillin. Table 1 summarizes data on the effect of the alkalinity of solution on the yield of vanillin and the rate of oxygen absorption in the oxidation of lignosulfonates.

A decrease in pH from 10.8 to 10.3 resulted in the dramatic inhibition of vanillin formation; however, it had almost no effect on the rate of oxygen absorption at 160°C. It is well known that the rate of oxidation of phenols and lignins decreases with decreasing pH because of a decrease in the degree of acidic dissociation. However, the absorption of oxygen for this reason was terminated at noticeably lower values of pH 9.0–9.5 [9]. Consequently, the inhibition of vanillin formation with decreasing pH was due to the acidic dissociation reactions of intermediates that are less acidic than phenols rather than due to the protonation of phenolic hydroxyl. In terms of mechanism (V)–(IX), this reaction is step (IX) of the retroaldol cleavage of substituted coniferaldehyde **XVI**. Note that this fact, which can be easily explained in terms of the proposed mechanism (Table 1), cannot be explained from the standpoint of other known hypotheses.

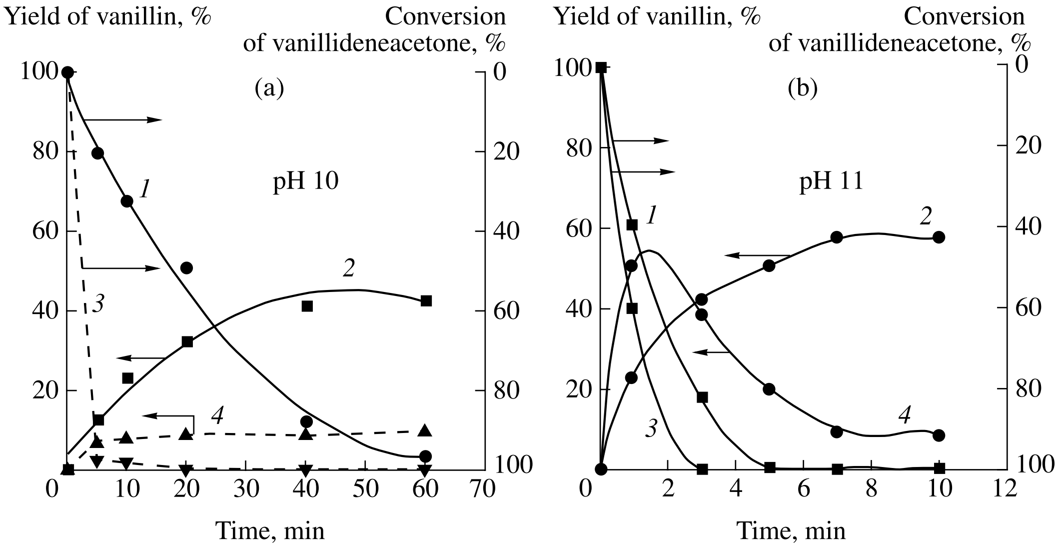


Fig. 1. Kinetic curves of (*1*, *3*) vanillideneacetone consumption and (*2*, *4*) vanillin buildup in an atmosphere of (*1*, *2*) argon or (*3*, *4*) oxygen in the presence of $Cu(OH)_2$ at pH (a) 10 and (b) 11. Reaction conditions: [vanillideneacetone] = 10 g/l; 160°C; $P_{Ar} = P_{O_2} = 0.3$ MPa.

To support the role of retroaldol cleavage in the formation of vanillin, we studied the kinetic behavior of vanillideneacetone (the simplest analog of coniferaldehyde) under conditions of lignosulfonate oxidation. In an argon atmosphere, vanillideneacetone was hydrolyzed to vanillin at pH 10 and 160°C for 30–50 min with ~90% selectivity for vanillin at the initial portion (Fig. 1). In the presence of oxygen and the catalyst, vanillideneacetone was consumed more rapidly by one order of magnitude, and the yield of vanillin decreased by a factor of 3–5 (Fig. 1a). This means that at pH 10 the rate of retroaldol cleavage is lower than the rate of vanillideneacetone oxidation to by-products; this is responsible for a considerable decrease in the yield of vanillin under the action of oxygen. The behavior changed as the pH was increased to 11 because of an increase in the rate of retroaldol cleavage, which is proportional to the concentration of the hydroxide ion [18]: the maximum yield of vanillin practically did not decrease under the action of oxygen, whereas the selectivity of its formation before a maximum was higher than 80% (Fig. 1b). It is evident that the yield of vanillin decreased after reaching a maximum concentration because of the subsequent oxidation.

Similar relationships between the yield of vanillin and the pH of the medium were also observed in the uncatalyzed oxidation of eugenol at 170°C (Fig. 2). A change from a 1 M NaOH solution to pH 10 resulted in a decrease in the yield of vanillin by a factor of 5–7. Thus, the effects of pH on the yield of vanillin in the oxidation of lignosulfonates, vanillideneacetone, and eugenol were absolutely analogous (Table 1 and Figs. 1, 2). This comparison demonstrates that the retroaldol cleavage of substituted coniferaldehyde **XVI** plays an important role in the oxidation of lignosulfonates, whereas it limits the process of vanillin formation at pH < 11.

Detection of postulated oxidation intermediates. In accordance with the postulated mechanism, coniferyl alcohol and coniferaldehyde, which are formed by the addition of the hydroxide ion to quinonemethide **XIII** under conditions of thermodynamic control, are the relatively stable molecular intermediates of eugenol oxidation [19].

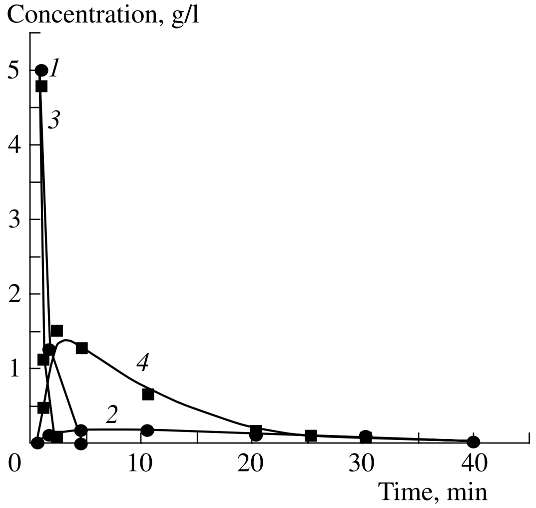


Fig. 2. Curves of (*2*, *4*) vanillin buildup and (*1*, *3*) substrate consumption in the oxidation of eugenol with molecular oxygen (*1*, *2*) at pH 10 and (*3*, *4*) in 1 M NaOH without a catalyst (160°C; [eugenol] = 5 g/l; $P_{O_2} = 0.3$ MPa).

Table 1. Effect of pH on the initial rate of oxygen consumption and parameters corresponding to the maximum concentrations of vanillin*

Entry	Base		Initial pH	Initial rate of O_2 consumption, g/min	Parameters corresponding to the maximum concentrations of vanillin		
	nature	concentration, g/l			[vanillin], g/l	time, min	final pH
1	NaOH	120	>13	0.080	13.9	40	9.9
2	NaOH	80	>13	0.115	10.7	20	11.0
3	NaOH + K_2CO_3	40 300	10.8	0.056	3.3	25	10.5
4	K_2CO_3	300	10.3	0.071	0.9	20	10.0

* Reaction conditions: T = 160°C; P_{O_2} = 0.2 MPa; [Cu(OH)$_2$] = 9.75 g/l; the dry solids content of the alkaline liquor was (entries 1, 2) 180 or (entries 3, 4) 120 g/l; pH was measured at 20°C.

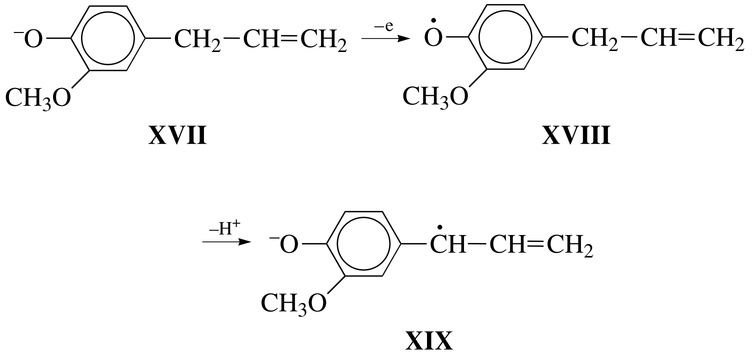
Table 2. Mass spectra of an eugenol oxidation intermediate (experimental) and coniferyl alcohol (database)

m/*e*	180	152	137	124	119	107	103	94	91	77	65	55
Peak intensity, % (experimental)	58	21	100	48	17	14	17	15	31	20	12	10
Peak intensity, % (database)	52	34	100	50	15	12	15	10	41	30	28	23

Indeed, coniferyl alcohol was systematically detected by chromatography–mass spectrometry in the oxidation of eugenol by copper oxide or oxygen in the presence of Cu(OH)$_2$ at 160–170°C. The experimental mass spectrum of a substance with *m*/*e* = 180 and the reference mass spectrum of *trans*-coniferyl alcohol from the database of a spectrometer coincide with a high degree of reliability (Table 2; the coefficient of correlation is $\rho = 0.91$).

EPR spectroscopy of intermediates in the oxidation of eugenol. The nature of primary radical intermediates in the oxidation of eugenol was studied by EPR spectroscopy. Figure 3 demonstrates the EPR spectrum of a radical, which was detected by the stopped-flow method in liquid nitrogen. The spectrum is a resolved doublet with the *g*-factor 2.0038 and the hyperfine splitting constant $a = 10.8 \pm 0.3$ Oe. We failed to detect the detailed hyperfine structure of the radical in the flow system at room temperature because of the formation of a paramagnetic resin at the walls of the flow cell.

The doublet structure of the signal is indicative of splitting due to one proton. The structure of phenoxyl radical **XVIII** obtained from eugenol (reaction (X)) contains only one proton that can give a doublet.



XVII **XVIII** **XIX**

(X)

This is the proton at the *ortho* position of the aromatic ring. The hyperfine splitting constant at *ortho* protons [20] is ~3–6 Oe. On the other hand, the hyperfine splitting constant of benzyl protons is 8–12 Oe [20]; however, the number of these protons in the structure of **XVIII** is two. A comparison of the experimental results and published data allowed us to attribute the observed EPR spectrum to the structure of radical anion **XIX**. It is well known that semiquinone radical anions are much more stable than neutral semiquinone radicals

[21]. From this standpoint, the detection of radical anion **XIX** is more probable than the detection of phenoxyl radical **XVIII** in the case that the former is formed in the course of oxidation.

The experimental results indicate that radical anion **XIX** is formed in the oxidation of eugenol, and the disproportionation of phenoxy radicals to quinonemethide **XIII** was not found. The formation of radical anion **XIX** by acidic dissociation (reaction schemes (VII), (X)) or hydrogen abstraction by a phenoxy radical from the phenoxy anion of a substrate is possible in terms of the energetics of these steps, as supported by quantum-chemical calculations [22].

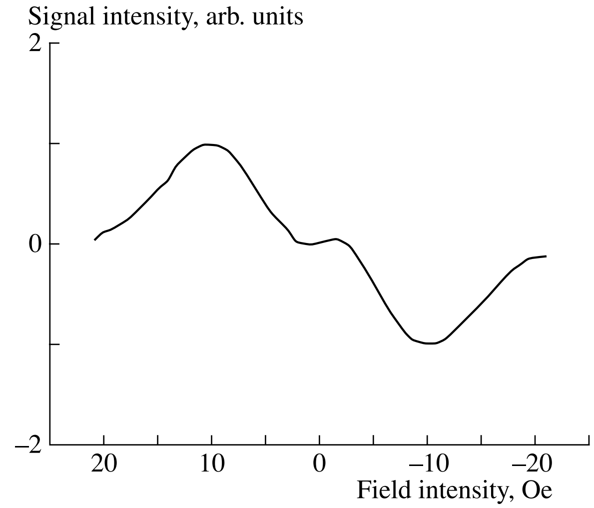
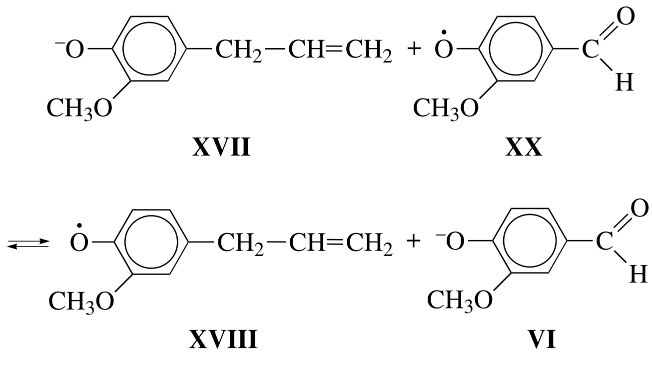


Fig. 3. EPR spectrum of eugenol oxidation intermediates.

Thermodynamic control of the process. Note that reaction mechanism (V)–(IX) and many other radical reactions of lignin conversion exhibit an important special feature: rapid and reversible electron exchange between phenoxyl radicals and anions can occur in these systems. Analogous electron transfer between semiquinone radicals and hydroquinone anions occurs at near-diffusion rates [23]. In this case, the ratio between the concentrations of molecular oxidation products (eugenol, coniferyl alcohol, coniferaldehyde, and vanillin) can depend not only on the kinetics but also on the thermodynamics of corresponding reactions. A considerable role of thermodynamic control was supported by the formation of vanillin rather than acetovanillone as the main product (see above). Thermodynamic control could also be responsible for the high selectivity of vanillin formation in the oxidation of eugenols and lignins, that is, a relatively low rate of aldehyde oxidation. In the oxidation of syringyl alcohol, the oxidation of the resulting syringaldehyde was observed only at an alcohol conversion higher than 90% [24]. A comparison of the one-electron oxidation potentials of eugenol, isoeugenol, coniferyl alcohol, and other phenols [25] demonstrated that donor substituents decreased the oxidation potential of compounds, whereas acceptor substituents increased this potential. This means that under conditions of thermodynamic control vanillin and syringaldehyde are relatively stable products in an oxidizing medium, as compared with eugenols and coniferyl alcohol. An analogous ratio between the oxidation potentials of phenoxyl radicals formed by substrate and product oxidation is no less important. It shifts an equilibrium to increase the yield of vanillin:



(XI)

Because the oxidation potential of vanillin phenoxy radical **XX** is higher than the potential of the radical that is formed by the one-electron oxidation of eugenol or lignins, equilibrium (XI) is shifted to the right. That is, under conditions of thermodynamic control, phenoxy radical **XX** acts as an oxidizing agent for the substrate with the regeneration of vanillin, if the latter is oxidized to the phenoxy radical in accordance with the reaction kinetics.

Chain mechanism of oxygen oxidation and process selectivity. The mechanism (V)–(IX) under consideration is a radical rather than chain mechanism. Consequently, a decrease in chain lengths in oxygen oxidation should increase the selectivity of vanillin formation. It is well known that the chain length decreases with increasing rate of initiation [26]. The step of initiation in the process under discussion is electron abstraction from phenolate ion **XI** by oxygen. From this standpoint, an increase in the rate of initiation due to an increase in the temperature and the pressure of oxygen should increase the selectivity of eugenol oxidation. Indeed, a decrease in the process duration from 60 min at 160°C to 2–5 min at 170°C and an oxygen pressure of 1 MPa increased the yield of vanillin in the course of catalytic oxidation with oxygen from 38 to 80–90 mol %. The resulting yields are almost threefold higher than the efficiency of the uncatalyzed process (Fig. 2).

The proposed mechanism and the experimental results demonstrate that the rate of oxidation should be increased using more severe reaction conditions in order to enhance the selectivity of lignin oxidation to aromatic aldehydes. Direct evidence in support of this conclusion with the use of the high-temperature oxidation of lignosulfonates and handwood as examples was presented in few publications [27, 28].

CONCLUSIONS

A critical analysis of published hypotheses concerning the mechanism of selective lignin oxidation to aromatic aldehydes in an alkaline medium revealed a number of disadvantages and contradictions. Thus, the well-known hypotheses are strictly specific for various oxidizing agents, and they do not explain the formation of aceto derivatives as by-products, the role of a strongly alkaline medium in the process, etc. A fundamental difference between the proposed mechanism and all the well-known hypotheses consists in the heterolytic nature of the key step of retroaldol cleavage of a bond between the α- and β-carbon atoms of the phenylpropane unit of lignin to form vanillin. In the well-known hypotheses, this bond cleavage occurs by homolytic oxidation mechanisms.

The mechanism considered in this work allows us to solve the above problems. Almost all steps of this mechanism (the formation of phenoxyl radical **XII** and quinonemethide **XIII** and the retroaldol cleavage of substituted coniferaldehyde **XVI**) are well known in the chemistry of lignin.

The proposed oxidation mechanism was supported by a number of experiments:

- Coniferyl alcohol was detected as an intermediate in the process of eugenol oxidation.

- The effect of pH on the kinetics of vanillin formation was of the same character in the oxidation of vanillideneacetone, eugenol, and lignin; this provides support for the role of retroaldol cleavage in the test processes.

- The compositions of the aromatic products of guaiacylpropanol and guaiacylethanol oxidation were fundamentally different; this fact is consistent with the proposed mechanism and cannot be explained in terms of other well-known hypotheses.

- The high rate and selectivity of the catalytic oxidation of eugenol to vanillin by oxygen under severe conditions provide support for the proposed nonchain radical mechanism of the reaction.

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