AUTOCATALYTIC PROCESSES DURING OXIDATION OF LIGNIN IN ALKALINE MEDIA

É. I. Chupka, V. N. Gvozdev, T. M. Rykova,
and O. V. Shadynskaya

Results are presented that characterize features of the oxidation of lignin in alkaline media. The prerequisites are considered and proofs are given of the appearance of autocatalytic reactions on the oxidation of lignin at the level of one-electron transfer between the phenoxyl radicals being formed and the initial fragments and between chromophores in triplet electronically excited states and other fragments and of the development of concerted oxidation reactions through the appearance of active forms of oxygen, and vibrationally excited states. The results obtained indicate that on the oxidation of lignin in alkaline media a network of chemical reactions bearing the autocatalytic nature of chain processes with degenerate energy branching is formed.

The combination of compositional inhomogeneity due to the presence of fragments differing in a wide range of oxidation and reduction potentials and having a globular structure and to the liberation of a considerable amount of energy on oxidation impart to the lignins a number of interesting kinetic features that have not previously been considered. These features are based on known laws that are typical for polymeric systems with well defined intramolecular electron-donor-acceptor and hydrogen bonds.

It is extremely important that these kinetic laws impose definite limitations on the interpretation of the results obtained with model compounds and their extrapolation to the properties and reactivity of lignin. A feature of the kinetics of the oxidation of lignin is the formation of a network of chemical reactions bearing the autocatalyic nature of chain processes with degenerate energy branching.

The special features of the kinetics of the oxidation of lignin are determined by a number of the most important factors and properties of the system:

1. The difference in the oxidation potentials of the initial fragments and of the products of their oxidation [1];

2. The chain mechanism of the oxidation of lignin [2];

3. The liberation of a considerable amount of heat on oxidation [3];

4. The chemical generation of electronically excited and vibrationally excited states;

5. The migration of electron excitation energy with the formation of new highly reactive centers (triplet states of the carbonyl groups of ketones, aldehydes, quinones, and quinonemethides), singlet oxygen [4];

6. The probability, on the radiationless deactivation of electronically excited states, which takes place in the interval of 10^{-3}-10^{-2} sec, of the localization of thermal energy in definite centers of the volume of the macromolecule with the formation of "microreactor" zones where the conditions are created for the thermal initiation of reactions the acceleration of which for each process takes place in accordance with the Arrhenius equation, i.e., the phenomenon of thermal autocatalysis is observed; and

7. The dissipation of thermal energy, leading to the appearance of vibrationally excited states and then to the cleavage of certain types of bonds.
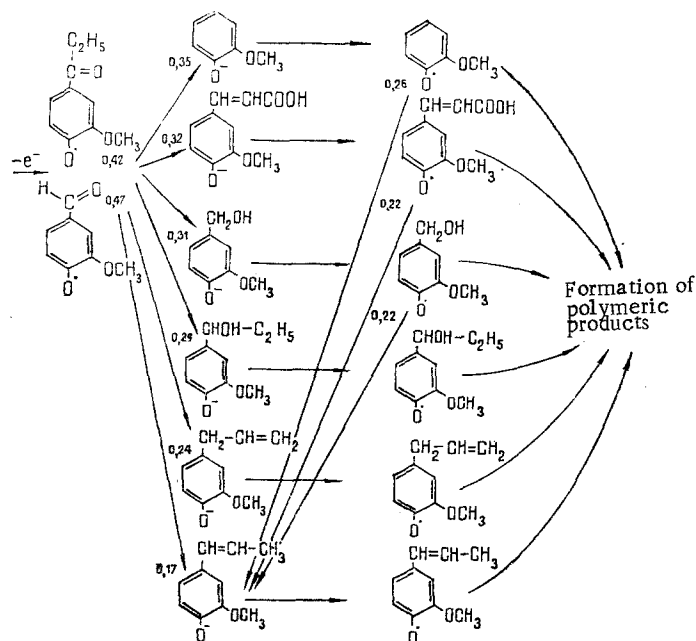

Fig. 1. Network of autocatalytic cross-reactions in
the oxidation of lignin at the stage of phenoxyl radi-
cals.

It is not difficult to observe that the above-mentioned properties and characteristics
are typical for oxidation processes proceeding by a chain mechanism with degenerate energy
branching that have been formulated by N. N. Semenov [5].

Let us consider what are the real prerequisites for the appearance of autocatalytic
reactions in the oxidation of lignin at the following levels:

— one-electron transfer between phenoxyl radicals being formed and the initial frag-
ments;

— between chromophores in triplet electronically excited states and between other
fragments;

— vibrationally excited States;

— the development of concerted oxidation reactions; and
— the appearance of active forms of oxygen the reactivity of which exceeds by several
orders of magnitude the rate of oxidation of phenols by molecular oxygen.

The presence of fragments with oxidation and reduction potentials differing by more
than 0.1 V predetermines the probability of electron transfer to considerable distances in
a current-conducting medium (solutions of alkalies). The donor and acceptor may then be
considered as half-cells of an electrochemical system between which there arises an emf
witnessing the occurrence of an exchange current. Electron-exchange reactions between a
number of phenols and phenoxyl radicals have been investigated in this way [6]. In view of
the rigid globular structure of the lignin macromolecule, a high probability of the migra-
tion of an electron within it may be assumed.

Using the method of cyclic voltammetry, we have investigated the oxidation potential
of a number of compounds modeling the structural unit of lignin and the reduction potential
of the corresponding phenoxyl radicals [7]. The results show that the phenoxyl radicals
formed on the oxidation of vanillin and of α-guaiacylpropanone are capable of oxidizing
practically all the model compounds studied, since the difference in the reduction potential
of the radicals and of the unoxidized fragments exceeds the threshold value of 0.1 V.

The phenoxyl radicals formed as the result of the one-electron oxidation of the other
lignin-modeling compounds that were investigated are, in their turn, capable of oxidizing
certain unoxidized initial fragments (for example, isoeugenol), while the recombination
of phenoxyl radicals leads to the formation of a polymer at the anode. The formation of
a polymer is also observed in the homogeneous oxidation of model compounds by O_2 and by K_3.

Fe(CN)$_6$ [8]. Figure 1 illustrates the network of autocatalytic cross-reactions arising on the oxidation of compounds modeling the structural unit of lignin at the stage of one-electron transfer with the formation of phenoxyl radicals. The numerical values of the oxidation potentials of the model compounds and the reduction potentials of the phenoxyl radicals formed are given the corresponding structures; the directions of the arrows reflect the route of electron transfer in the donor-acceptor pairs.

Thus, on combined oxidation, through the recombination of various radicals a copolymer of complex structure will be formed the composition of which is determined by the concentrations of the initial forms, the rate of their oxidation, and the rate of recombination of the phenoxyl radicals. Consequently, the results presented show that a network of autocatalytic cross-reactions arises already at the stage of one-electron oxidation. It is quite obvious that the formation of products at the level of two-electron oxidation (aldehydes, ketones, quinones, quinonenethides, and quinol peroxides) will considerably complicate the network of chemical reactions.

The first one-electron transfer in the oxidation of phenols is an endothermic reaction taking place with an activation energy of 105—150 kJ/mole, depending on the structure of the phenol [9]. The rate constant of the oxidation of phenols by oxygen with the formation of phenoxyl radicals, K, amounts to 10^{-10} liter/mole^{-1}·sec-1 (T = 25°C). The phenoxyl radicals then react with O_2 with a rate constant of 10^3 liter^2/mole^2·sec, i.e., several orders more vigorously than in the initial oxidation of the phenols [10]. This explains the low steady-state concentration of radicals that is usually observed in the oxidation of lignin. The nature of the reacting radicals is dynamic, since their species composition changes with time as a result of the stepwise oxidation process.

Then the oxidation process aquires a chain mechanism, the orders of the reaction in the kinetic equation being (n = 3/2) for lignin and (n = 1/2) for oxygen with bimolecular chain termination, apparently through the reaction RO$_2$ + RO$_2$ [11]. Chain propagation may be due to the interaction of the phenoxyl radicals with molecules of the initial ccompounds.

Phenoxyl radicals react with peroxide radicals with a rate constant of 10^9 liter·mole^{-1}·sec^{-1} [12] to form quinol peroxides;
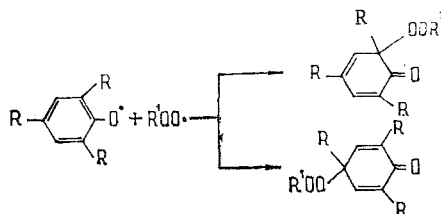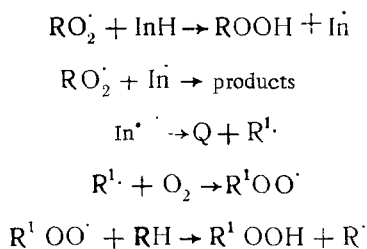

which are stable at low temperatures but at temperatures above 100°C rapidly break down into radicals that become oxidation initiators [13].

For phenoxyl radicals with alkoxy substituents in the para position a chain-propagation reaction by the following scheme [9] is possible
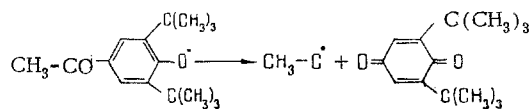
The mechanism of inhibited oxidation (the case of alkaline cooks with additives) includes the following stages:

$$RO_2^{\cdot} + InH \rightarrow ROOH + \dot{In}$$

$$RO_2^{\cdot} + \dot{In} \rightarrow products$$

$$In^{\cdot} \rightarrow Q + R^{1\cdot}$$

$$R^{1\cdot} + O_2 \rightarrow R^1 OO^{\cdot}$$

$$R^1 OO^{\cdot} + RH \rightarrow R^1 OOH + R^{\cdot}$$

As the result of the recombination of peroxide radicals the process acquires an exothermic nature and is accompanied by the liberation of thermal energy and by the formation of aldehydes and ketones in the triplet electronically excited state [2]. At this stage, a new level of autocatalytic reactions arises. In view of the globular structure of the lignin macromolecule, we are justified in assuming that at the foci of formation of triplet electronically excited aldehydes, ketones, and alcohols their rapid deactivation in the course of $10^{-9}-10^{-2}$ sec leads to the situation that the thermal energy, not having time to be dissipated, provides the zone of a "microreactor" with elevated temperatures relative to the mean temperature of the system and creates conditions for the thermal autocatalysis of a group of chemical reactions in accordance with the parameters of their individual Arrhenius equations. The thermal energy liberated in the process of the radiationless deactivation of electronically excited states in the oxidation of lignin is utilized not only in processes of thermal autocatalysis by raising the rate constants of chemical reactions according to the temperature but also in the generation of vibrationally excited states.

The energy of excitation of vibrational levels is substantially smaller than the energy of excitation of electronic levels. Vibrational excitation can therefore affect processes having low activation energies comparable with the energy of vibrational transitions, which include a broad class of reactions of molecules with free radicals [14].

In the oxidation of lignin 110-241 kJ/mole of energy is liberated (the mass of a phenylpropane structural unit was taken as one mole) [3]. The energies of vibrational excitation of individual bonds are given in Table 1 [15]. The results show that the energy liberated is more than sufficient for the vibrational excitation of a number of types of bonds that are characteristic for lignin. This energy is sufficient for the thermal dissociation of —O—O— bonds in peroxides and hydroperoxides (120-160 kJ) [5] and, consequently, for beginning oxidation initiated by peroxide decomposition products.

The possibility of the development of concerted reactions under the conditions of alkaline methods of delignification was predicted by D. V. Tishchenko [16]. However, because of the complexity of the material, direct experimental investigations are difficult. The probability of their occurrence has nevertheless been convincingly demonstrated on compounds modeling the structural unit of lignin. The influence of additions of α-guaiacylpropanol and isoeugenol on the oxidation of vanillin has been investigated with the aid of a micromammnometric method [11]. It follows from the results obtained that these additions considerably increase the rate of consumption of oxygen by the vanillin, i.e., they accelerate the oxidation of the vanillin.

Thus, the results obtained show that the combined oxidation of vanillin and α-guaiacylpropanol, and of vanillin and isoeugenol, is characterized by the occurrence of concerted reactions. Consequently, concerted reactions also take place in the lignin macromolecule and may be considered as a case of autooxidation.

The formation of electronically excited triplet states of compounds containing carbonyl groups (structures of the type of vanillin, α-guaiacylpropanone, quinones, and quinonemethides) leads to the appearance of a new network of oxidation reactions between electronically excited fragments possessing electron-acceptor properties and fragments in the ground state possessing electron-donor properties. Thereupon a quenching of the intensity (I) of the phosphorescence of the lignin chromophores is observed that takes place at different rates according to the structures of the irradiated chromophore and of the quenching agent. Quenching takes place by a chemical charge-transfer mechanism and represents a redox reaction occurring without the participation of oxygen.

We have singled out schemes known from the literature [17] for the formation of the main carbonyl-containing chromophores of ligning that must be present in triplet excited states and have investigated the quenching of the intensity of the phosphorescence of lignin and some other chromophores by means of compounds modeling the structural unit of lignin and of carbohydrates.

The results show that the phosphorescence of vanillin, of rosolic acid, and of previously oxidized Pepper lignin is intensively quenched by fragments possessing electron-donating properties in relation to these states and by carbohydrates in accordance with the Stern—Volumer equation $I_0/I = 1 + K_{e\tau}$ [Q] (the electron-donor-acceptor pairs were selected so as to exclude possible quenching by a physical mechanism). The quenching of the phosphorescence takes place with no change in lifetime, which is one of the items of evidence in favor of a tunnel mechanism of electron transfer.

TABLE 1. Energies of the Stretching Vibrations of Various Types of Bonds

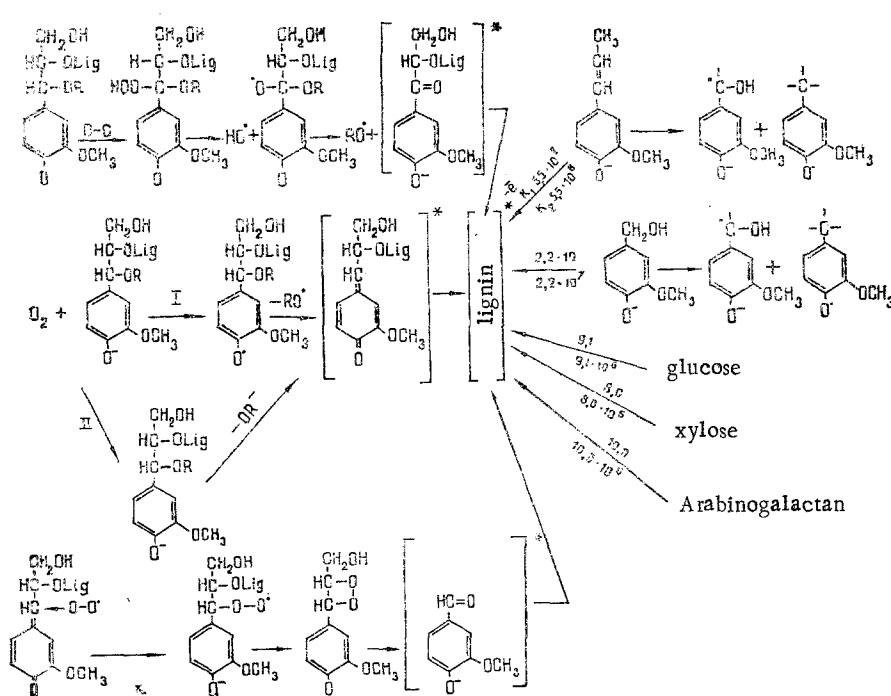| Type of bond	Type of structure	Energy, kJ
O — O	Peroxides	10 ÷ 12
C — O	Primary alcohols	12,2 ÷ 12,5
C — O	Secondary alcohols	12,9 ÷ 13,1
C — O	Methoxyls	13,4 ÷ 13,6
C — O	Phenols	14,4 ÷ 14,7
C — O — C	Ether bond	15,2 ÷ 1,5
C = C	Aromatic ring	17,9 ÷ 18,1
C — C	Aromatic ring	19,1 ÷ 19,2
C = C	Nonaromatic structures	19,3 ÷ 19,5
C = O	Conjugated	19,8 ÷ 20,0
C = O	Quinones	20,2 ÷ 20,3
C = O	Nonconjugated	20,4 ÷ 20,6

Fig. 2. Scheme of the formation of electronically excited states of carbonyl-containing lignin chromophores and rate constants of electron transfer in the solid phase (T = 77K; 7 N NaOH) (K_1) and in the cooking process (K_2, liter/mole·sec) between various lignin fragments and carbohydrates.

A similar tendency to the acceptance of an electron in the absence of an oxidizing agent is shown by the products of the oxidation of carbohydrates, with an emission maximum in the 480 nm region and a lifetime τ = 0.33 sec. The superposition of the energy and time characteristics of lignin oxidation products and of carbohydrate decomposition products predetermines the possibility of the transfer of energy between them. The quenching of the fluorescence of the products of the oxidation of glucose and of oxidized Pepper lignin by a stable nitroxyl radical is evidence in favor of the assumption that the triplet states of lignin fragments containing carbonyl groups are biradical states.

Thus, the quenching of phosphorescence by electron-donating fragments indicates the appearance of a network of chemical cross-reactions between an electron donor and an electron acceptor that is in the excited triplet state at the moment of formation, on the one hand, and other lignin fragments (Fig. 2) and carbohydrates (Fig. 3), on the other hand. On the
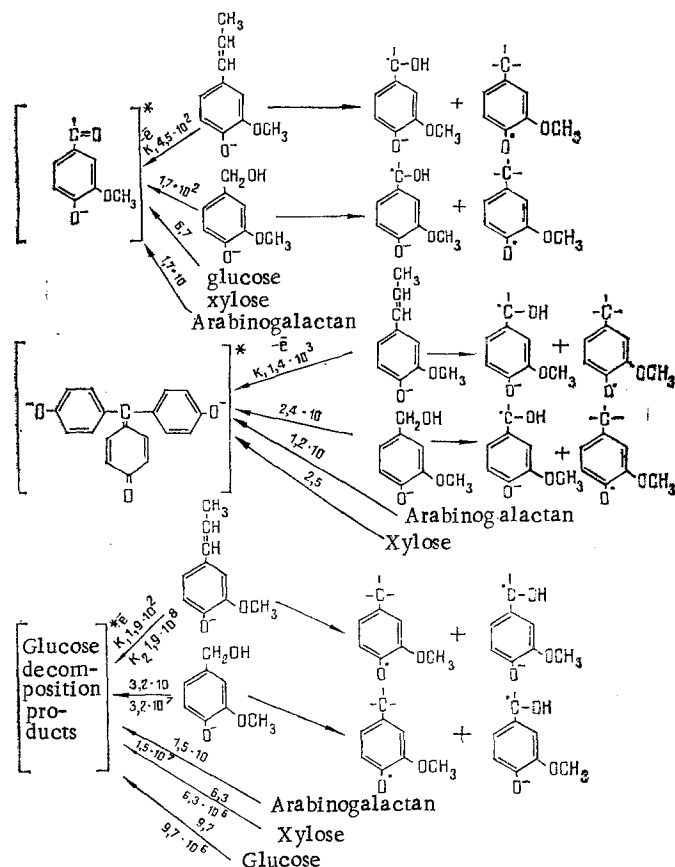
Fig. 3. Scheme of the interaction of electronically
excited states of carbonyl-containing fragments of the
structural unit of lignin and of carbohydrate decom-
position products with other lignin fragments and car-
bohydrates, and the rate constants of electron transfer
in the solid phase (T = 77K; 7 N NaOH) (K_1) and in the
cooking process (K_2, liter/mole·sec).

oxidation of electron-donating fragments by a triplet-excited acceptor, they can be generated
by lignin fragments, by carbohydrates, and by the products of their decomposition, which
explains the feeble intensity of the chemiluminescence and its increase on the addition of
activators that ensure the transfer of energy to themselves, promoting the deactivation of
the energy donor and lowering the probability of its participation in redox reactions [19].

It must be borne in mind that, thanks to their high reactivity and in view of the associa-
tion in one system of fragments with different donor-acceptor properties, the steady-state
concentration of triplet states in lignin cannot be considerable; nevertheless it is respon-
sible for a whole complex of oxidative reactions taking place via electronically excited
states.

The facts presented on features of the oxidation of lignin, the generation of active
centers as a result of the migration of the energy of electronic and vibrational excitation,
their reactivity in redox reactions, and the redistribution of thermal energy correspond
to all the main characteristics of chain processes with degenerate energy branching in which
a definite role is played by non-steady-state excited levels.

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NEW SYNTHESIS OF [8-ARGININE] VASOPRESSIN AND ITS DE-9-GLYCINE ANALOGS

O. S. Panseuvich, G. I. Chipens,
A. O. Korps, and A. P. Pavar

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A unified scheme is proposed for the synthesis of [8-arginine]vasopressin (I), de-9-glycine[8-arginine]vasopressin (II), and de-9-glycinamide[8-arginine]vasopressin (III) which has been developed on the basis of the tetrapeptide Gln-Asn-Cys(Bzl)-Pro and other homologous fragments of neurohypophyseal hormones as common initial and intermediate compounds. The free dithiols obtained by the reduction of protected derivatives of (I)-(III) by sodium in liquid ammonia have been oxidized to the corresponding cyclic disulfides (I)-(III) with the aid of 1 M H_2O_2 at 0-5°C and pH 8.5. The vasopressor activities of (I)-(III) are, respectively 470 ± 20, 1.7, and 0.5 IU/mg (rat, in vivo).

In view of the high degree of homology of the primary structures of the neurohypophyseal hormones, great interest is presented by unified schemes for their synthesis using a whole series of common initial and intermediate compounds. For the synthesis of arginine- and lysine-vasopressins, oxytocin, and vasotocin, and also their analogs modified in the C- and N-ends of the peptide chain, one such intermediate compound may be the tetrapeptide of sequence 4—7, which is the longest common structural fragment of these hormones. A scheme (in two variants) using Gln-Asn-Cys(Bzl)-Pro for the synthesis of [Phe[2], Orn[8]]vasopressin has been described previously [1]. The aim of the present work was the synthesis from this tetrapeptide of arginine-vasopressin (I) and two of its analogs — de-9-glycine[8-arginine]·vasopressin (II) [2, 3] and de-9-glycinamide[8-arginine]vasopressin (III) [4, 5].