FEATURES OF THE INITIAL STAGES OF THE OXIDATION OF LIGNIN BY HYDROGEN PEROXIDE

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The kinetics of the initial stages of the oxidation of lignin and of several model compounds have been studied by the stopped-jet method. It has been shown that in the initial stage an intermediate compound is formed with an absorption spectrum close to that of phenoxyl radicals and with a lifetime of 0.013 sec. The high reactivity of the intermediate products leads to a branching of the oxidation process.

In publications on the oxidation of lignin [1, 2] that is no information on the initial, fastest, stages of the oxidation process. One of the most useful methods in investigating the initial stages of the oxidation of phenols is the stopped-jet method with spectral recording [3]. We have attempted, using this method, to follow the kinetics of the initial stages of the oxidation of lignin and of some model compounds.

When lignin is oxidized with hydrogen peroxide in the time interval of 0.05-0.1 sec the optical density of the solution increases (Fig.1, curve 1). The absorption spectrum of the intermediate product (I) (Fig. 2, curve 1) has a maximum at λ 412 nm, a shoulder at 430-440 nm, and diffuse maxima at λ 460-470 nm and 490-500 nm. The form of the spectrum coincides with that of phenoxyl radicals [4]. Consequently, it may be assumed that the kinetic curve (Fig. 1, curve 1) corresponds to the destruction of the phenoxyl radicals formed as the result of the one-electron oxidation of lignin fragments. The stage of the formation of phenoxyl radicals cannot be distinguished on the kinetic curve. The destruction of the intermediate product takes place by a first-order reaction (Fig. 1, curve 3) with a rate constant $K_{\text{des}} = 74.5$ sec^{-1}.

The anamorphosis of the kinetic curve 1 (the curve passes through a minimum) indicates the accumulation and destruction of another intermediate product, (II), the absorption spectrum of which (Fig. 2, curve 2) has maxima at λ 420 nm and 470-480 nm and a diffuse maximum with λ 510-530 nm. The accumulation of (II) takes place by a first-order reaction with a rate constant $K_{\text{form}} = 45.3$ sec^{-1}, and its destruction by a second-order reaction with a half-transformation time $\tau_{1/2} = 5.1$ sec (at a lignin concentration of $3 \cdot 10^{-3}$ nominal moles/liter).

When lignin is oxidized, there is also evidence of the formation and destruction of an intermediate product (III) which has an absorption maximum in the region of λ = 600 nm (Fig. 1, curve 3). The accumulation of (III) takes place by a first-order reaction with a rate constant $K_{\text{form}} = 58$ sec^{-1}, and the destruction of the product by a second-order reaction with a half-transformation time $\tau_{1/2} = 25$ sec (at a lignin concentration of 10^{-2} nominal moles/liter).

The dependence of the optical densities of both the first and the second intermediate products on the concentration of lignin (Fig. 1, curve 1, sections A and B) are linear in logarithmic coordinates (Fig. 3).

On the oxidation of model compounds of the structural unit of lignin (α-guaiacylpropanol, α-guaiacylpropanone, ferulic acid), as in the oxidation of lignin, an increase in the optical density in the λ 415 nm region was recorded. On the kinetic curves of the oxidation of α-guaiacylpropanol and α-guaiacylpropanone (Fig. 4) a stage can be traced of the accumulation of phenoxyl radicals and a stage of their destruction. In the case of ferulic acid, just as that of lignin, the formation stage is indistinguishable. Consequently, in lignin, there are groups oxidizing at a high rate in comparison with α-guaiacylpropanol and α-guaiacylpropanone.

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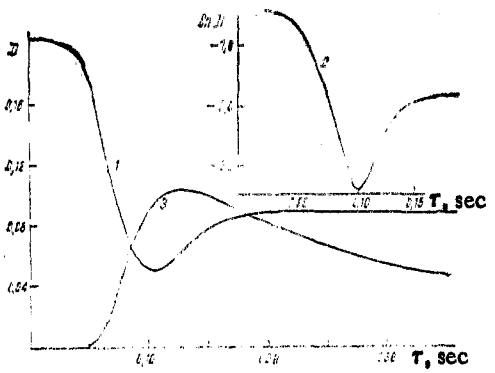

Fig. 1

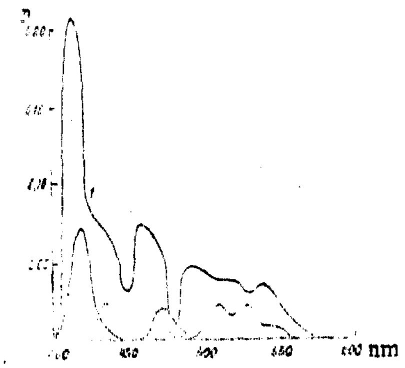

Fig. 2

Fig. 1. Change in optical density with time: 1) λ = 415 nm; 2) semilogarithmic anamorphosis of curve 1; 3) λ = 600 nm.

Fig. 2. Absorption spectra of the intermediate products: 1) τ = 0.025-0.1 sec; 2) τ ≥ 0.1 sec.

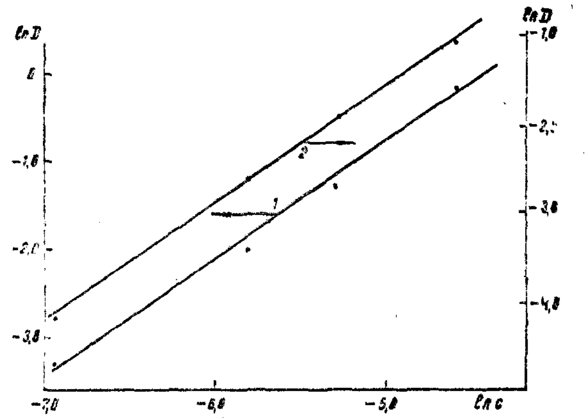

Fig. 3

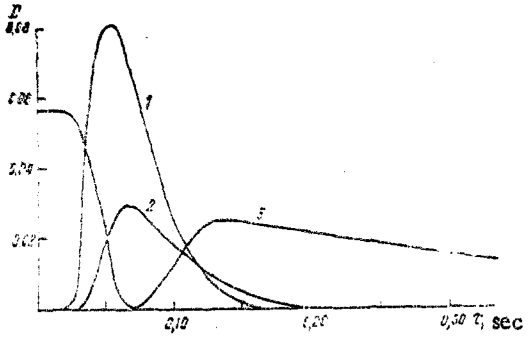

Fig. 4

Fig. 3. Dependence of the optical density on the concentration of lignin at λ = 425 nm: 1) τ = 0.025 ±0.1 sec; 2) τ > 0.1 sec.

Fig. 4. Change in the optical density with time in the oxidation of α-guaiacylpropanol (1), α-guaiacylpropanone (2), and ferulic acid (3) (λ = 415 nm).

On the basis of the results obtained, it is possible to suggest the following scheme for the initial stages of oxidation:

$$\begin{tikzcd}
 & & C_1 \arrow[r] & D_1 \\
L \arrow[r] & R \arrow[ur] \arrow[dr] & & \\
 & & C_2 \arrow[r] & D_2,
\end{tikzcd}$$

where L represents lignin; R represents a phenoxyl radical; C_1, C_2 are intermediate products; and D_1, D_2 are the final products of the oxidation of lignin.

EXPERIMENTAL

Dioxane lignin according to Peper was isolated as described in the literature [5]. Oxidation was carried out in 1 M NaOH and at a lignin:peroxide ratio of 1:100. The dynamics of the oxidation process were studied with the aid of a RMA-1A Rapid Mixing Attachment Stopped-Jet device and a Shimadzu UV-300 double-beam recording spectrophotometer. Recording was carried out with the aid of a Data Processing Sapcom-1 microprocessor with output to a recorder. The time of mixing was 1 msec.

SUMMARY

1. In the initial stages of the oxidation of lignin, intermediate products having spectra close to those of phenoxyl radicals with a half-transformation time $\tau_{1/2} = 0.013$ sec are formed.

2. Lignin contains groupings that are more readily oxidized than α-guaiacylpropanol.

3. The high reactivity of the intermediate products leads to a branching of the oxidation process.

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NEW DERIVATIVES OF 18-CROWN-6 CONTAINING A METHYLINDANONE FRAGMENT IN THE RING

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New derivatives of 18-crown-6 containing a methylindanone fragment in the ring have been obtained by the acylation of dibenzo-18-crown-6 with unsaturated acids in the presence of polyphosphoric acid.

We have previously developed a new method of obtaining derivatives of benzocrowns with attached side chains with the aid of acylation and alkylation reactions in the presence of polyphosphoric acid (PPA). Mono- and dicarboxylic acids were used as acylating agents, and alcohols as alkylating agents [1, 2].

In the present paper we consider the preparation of derivatives of 18-crown-6 containing a methylindanone fragment in the ring as a structural subunit. The synthesis of such compounds proved to be possible by using unsaturated acids in the acylation of dibenzo-18-crown-6.

The acylation of phenol and of anisole with methacrylic acid in the presence of $AlCl_3$ is accompanied by alkylation, i.e., ring-closure of the unsaturated ketone in the meta position, as a result of which 2-methyl-5-hydroxyindanone or the corresponding 5-methoxy compound is formed [3]. (Scheme, top, following page.)

We have performed the acylation of dibenzo-18-crown-6 with α-crotonic and methacrylic acids in the presence of PPA. In each case, the reaction took place quantitatively at 70°C in 4 h with the formation of almost identical amounts of the mono- and disubstituted derivatives. The reaction with methacrylic acid was carried out in the presence of a polymerization inhibitor — hydroquinone. The reaction products were separated by repeated column chromatography on alumina. The structures of the products isolated were shown with the aid of spectral methods (PMR, IR, and mass spectra). The disubstituted derivatives consisted of mixtures of structural isomers differing in melting points and solubility and in the form of the multiplet of the methylene protons of the macrocycle in their PMR spectra. For simplicity of discussion, we shall arbitrarily call the low-melting isomer the "trans" and the high-melting isomer the "cis" isomer, by analogy with the structures demonstrated previously for the isomers of 4',4"- and 4',5"-diacetyldibenzo-18-crown-6's [1].

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