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ENZYMATIC OXIDATION OF LIGNIN AND OF COMPOUNDS MODELING IT. IV. CHARACTERISTICS OF THE CHEMILUMINESCENCE ON PEROXIDASE OXIDATION OF α-GUAIACYLPROPANONE

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We have previously established that the peroxidase oxidation of lignin and of a number of its phenylpropane structures, including α-guaiacylpropanone, takes place through a stage of the formation of excited intermediates the deactivation of which leads to an emission of radiation in the visible region of the spectrum – chemiluminescence (CL) [1, 2]. The emission spectra of the excited chromophores of lignin [3] and of a number of its structural units are practically identical (Fig. 1), which points to a similarity of the mechanisms of the deactivation of the excited intermediates. The appearance of radiation in the red region of the spectrum (λ_{max} 630 nm) is explained by the formation of singlet oxygen in the system. Emission in the 560-nm region is connected with the radiative deactivation of a carbonyl group in the excited triplet state. It is still not clear whether it is the carbonyl group of the substrate present in the α-position that is excited or whether, in the process of peroxidase oxidation, quinones (of the p-quinone type) are formed, the excited carbonyl groups of which also radiate in the 560-nm region on deactivation [4].

In spite of the identity of the emission spectra, the deactivation of the excited chromophores formed on the peroxidase oxidation of α-guaiacylpropanone has a number of characteristic features which appear in an analysis of the kinetic curves of the quenching of the CL. The kinetic curve of CL on the peroxidase oxidation of lignin is characterized by a sharp flash of light followed by an exponential dying away of the radiation [1]. In contrast to the peroxidase oxidation of lignin, the kinetic curve of the CL on the oxidation of α-guaiacylpropanone has two maxima of the intensity of emission. In the first stage of the process, during a time of less than 20 sec, the intensity of emission rises rapidly from 0 to I_{init} (Fig. 2). The time to reach the first maximum and its intensity are determined by the concentration of peroxidase. In the second stage of the process, after some fall in emission, there is a slower rise in intensity to a maximum (I_{max}) and a subsequent dying away of the radiation.

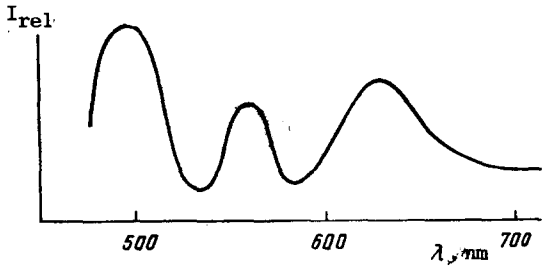

Fig. 1. Radiative deactivation spectrum of excited intermediates from α-guaiacylpropanone.

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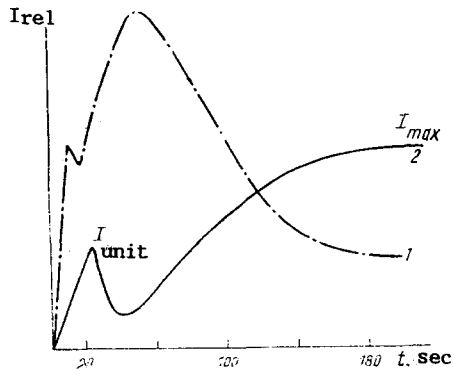

Fig. 2. Kinetic curves of the CL arising in the peroxidase oxidation of α-guaiacylpropanone. Concentrations of peroxidase: 1) $2 \cdot 10^{-6}$ M; 2) $2 \cdot 10^{-7}$ M; of H_2O_2: 0.09 M; and of the substrate: 10^{-2} M.

A lowering of the concentration of the substrate leads to a disappearance of the first maximum.

The amount of hydrogen peroxide does not affect the form of the kinetic curve of the CL. The intensity of the second maximum is twice that of the first ($I_{max} = 2I_{init}$), and this ratio is retained with variations in the concentrations of peroxidase and of H_2O_2.

A similar phenomenon has been observed in a study of the spontaneous biochemiluminescence of lipids on the addition of an excess of bivalent iron ions [5]. The authors explain the first fast maximum of the CL by catalysis of the decomposition of hydroperoxides with the formation of free radicals and by an acceleration of free-radical oxidation. The second, slowly developing, maximum is determined by the initiation of free radicals on the interaction of the bivalent iron with oxygen. In the opinion of the authors concerned, catalysis is exhibited only by bivalent iron ions, and their transformation into Fe^{3+} leads to a cessation of catalysis.

Since an iron ion is a component of the active site of peroxidase ($Fe^{2+} \leftrightarrow Fe^{3+}$) it is completely probable that an analogous process occurs in the peroxidase oxidation of α-guaiacylpropanone.

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