CHANGE IN THE CONCENTRATION OF FREE RADICALS ON THE PHOTOLYSIS OF LIGNIN

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It has been shown that under the action of UV light on solid preparations of lignin the generation of electron paramagnetic centers (EPCs) takes place, their concentration rising with a fall in the wavelength of the exciting light. In a dark stage there is a slow "death" of EPCs with time. The reactivities of individual model compounds of lignin in radical reactions in solutions were followed with the aid of a stable nitrogen radical used as a spin label. The results show that the efficiency of quenching differs considerably for individual chromophores and decreases in the sequence benzoquinone, vanillin, quinone methide, Björkman lignin, and soda lignin. The change in the concentration of EPCs of the stable radical with time is described by a first-order equation.

Investigations in the field of the photochemistry of chromophores of lignin will unite problems connected with the change in the color of cellulosic materials due to photochemical transformations of the lignin chromophores, permit an estimation of the possibility of the photoinitiation of the grafting of various monomers with the aim of modifying the properties of wood pulps, and substantially add to our knowledge of the role of the phenolic compounds of the cambial layer in protection from radiation.

We have studied the dynamics of change in the concentration of electron paramagnetic centers (EPCs) in Björkman lignin on photointeraction with individual sections of the spectrum of a DRL-1000 lamp, isolated with the aid of liquid filters on solid preparations, and the change in the concentration of EPCs in the photolysis of lignin and some model compounds in solution [ethanol—dioxane (1:1)] and with the use of the radiation of a LGI-21 laser λ_{exc} = 337 nm).

In an analysis of dry preparations, Björkman pine lignin was placed in a quartz capillary and was irradiated with the light of a DRL-1000 lamp through filters. The change in the concentration of EPCs was determined by the use of a EPA-2M electron paramagnetic analyzer. The concentration of free radicals was determined from the formula

$$N_x = N_{st} \cdot \frac{I_x \cdot H_x}{I_{st} \cdot H_{st} \cdot m} \text{ (spins/g)},$$

where I_x and H_x are the intensity and field strength of the ESR signal of the sample under investigation, relative units; I_{st}, H_{st}, corresponding respective values for the standard; N_{st}, concentration of EPCs for the standard; and m, weight of the sample under investigation, g.

The light stage (L) is characterized by a relatively rapid accumulation of EPCs in solid lignin preparations to some limiting cncentration which, like the intensity of the signal, rises with a decrease in the wavelength of the exciting light (Fig. 1).

The ESR spectrum consists of a singlet with ΔH between 8 and 12 Oe (Fig. 2).

In the dark stage (D) a slow "death" of the EPCs with time is observed (only after a day did the concentration of EPCs in the preparations reach the initial value). The process of "death" of the EPCs in the dark stage is described by a second-order kinetic equation, as is shown by the linear relationship in the coordinates $1/N_x = f(\tau)$.

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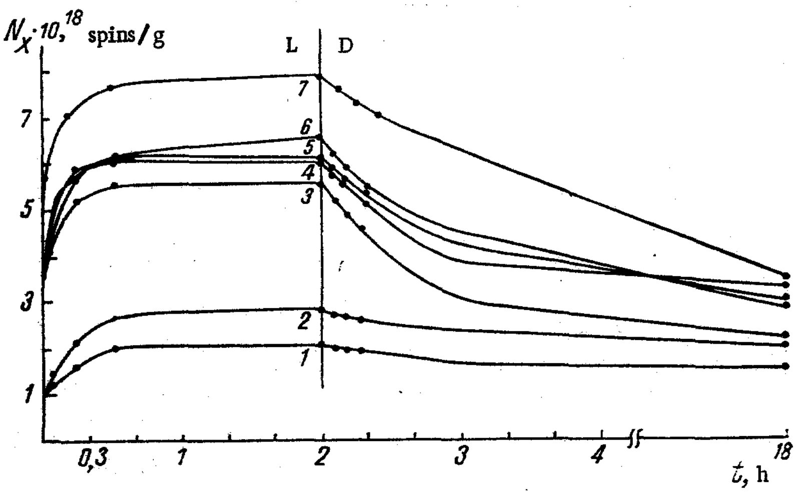


Fig. 1. Change in the concentration of EPCs in lignin on photosensitization with different wavelengths: 1) $\lambda_{50\%}$ = 490 nm, 2) 435 nm, 3) 320 nm, 4) 290 nm; 5) 250 nm; 6) 220 nm; 7) 195 nm (L, light; D, dark stage).

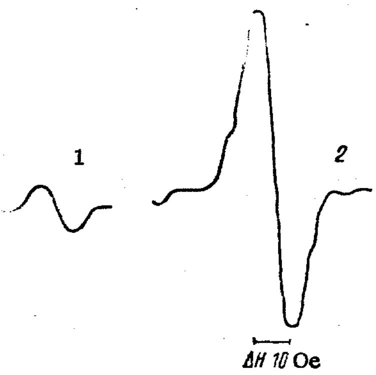
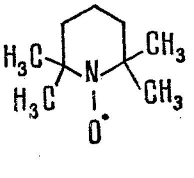


Fig. 2. ESR spectrum of the initial (1) and irradiated (2) Bjorkman lignin.

Thus, the decrease in the concentration of EPCs in the dark stage is, in all probability, due not to deactivation of the triplet states of the chromophores (1st-order process) but to a slow recombination of radicals to form the products of the photochemical reactions complicated by spatial effects in the solid matrix.

The photolysis of model compounds — vanillyl alcohol, vanillin, isoeugenol, guaiacol, and benzoquinone — was accompanied by a change in the chromophoric composition but no formation of EPCs was recorded under the conditions of the experiment. No changes in the concentration of EPCs was observed, either, in photolysis of lignin and model compounds in solutions in dioxane—ethanol (1:1), dimethyl sulfoxide, dioxane, dimethylformamide, or hexametapol on irradiation with light from a LGI-21 laser.

It is difficult to assume that the photolysis of lignin in solutions takes place without a stage of the formation of EPCs, i.e., in a direction qualitatively different from that in the solid state. However, the occurrence of radical processes in the photolysis of lignin and the reactivities of the individual model compounds in radical reactions in solutions can be judged from the decrease in the concentration of a radical used as a spin probe that is stable to the action of light of the given frequency [1]. As spin probe we used a nitroxyl radical (Rozantsev's radical):



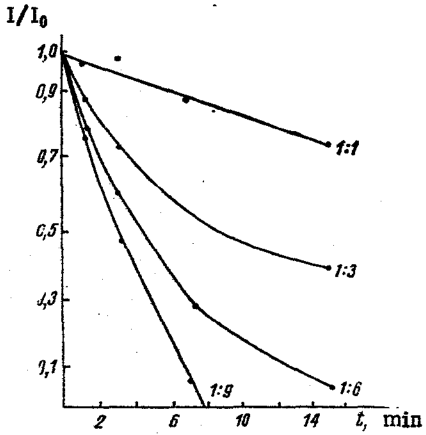


Fig. 3

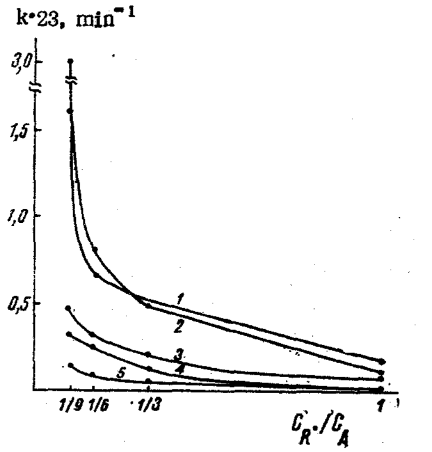


Fig. 4

Fig. 3. Relative change in the intensity of the ESR signal on photolysis with time at various concentrations of vanillin.

Fig. 4. Dependence of K_{eff} of the quenching of the signal of a stable radical on the concentration of acceptor; 1) benzoquinone; 2) vanillin; 3) rosolic acid; 4) Björkman lignin; 4) soda lignin. ($C_{R\cdot}$, concentration of stable radicals; C_A, concentration of acceptor).

The concentration of EPCs of this radical in the time interval studied in solution [ethanol–dioxane (1:1)] with irradiation at λ_{exc} = 337 nm (LGI-21 laser) remained unchanged, which shows its stability. The addition to a solution of the nitroxyl radical of benzoquinone, vanillin, rosolic acid (aquinone methide) and samples of lignin led on irradiation to a decrease in the intensity of the stable radical with retention of the form of the signal (triplet with an intensity ratio of 1:1:1).

The "quenching" effect is determined by the concentration and form of the added acceptor and is observed only when the mixture is irradiated. (In a control experiment with the addition of the compounds under investigation in the dark stage no quenching was observed.)

Figure 3 shows the relative change in the intensity of the ESR signal of the stable radical on photolysis with time at various concentrations of vanillin in the mixture. Similar relationships were obtained for the other compounds investigated. The results show that fragments containing a carbonyl group (as is well known, a group readily passing into the triplet state), quinones, and lignin preparations in the excited state are acceptors in relation to the spin probe. The change in the concentration of EPCs of the Rosantsev radical with time is described by a first-order equation in which the proportionality coefficient (K_{eff}) depends on the ratio of concentrations of the radical of the probe and of the acceptor. This provides the possibility of evaluating the efficiency of the quenching of the signal of the nitroxyl radical by individual acceptors.

The dependence of the rate constant of the quenching of the EPC signal of the nitroxyl radical on the $C_{R\cdot}/C_A$ ratio for the compounds investigated is shown in Fig. 4.

The efficiency of quenching differs considerably for individual chromophores and decreases in the sequence benzoquinone, vanillin, quinone methide (rosolic acid), Björkman lignin, soda lignin.

The quenching of the intensity of the signal of the free probe by the model compounds is accompanied by an act of recombination, since when irradiation was stopped the intensity of the EPC signal of the spin sound did not return to its original level.

Thus, the photolysis of lignin in the solid state and in solution takes place with the formation of EPCs, the reactivity of which differs considerably for the individual chromophores. To monitor the formation of EPCs in solutions on photoexcitation Rozantsev's stable radical can be used as a label.

LITERATURE CITED

1. Free Radicals in Biology [in Russian], Moscow, Vol. I (1979), p. 178.