To check the hypothesis of the formation of $O_2^{\cdot -}$ we have studied the autooxidation of lignin in an aqueous organic medium [universal buffer, pH 9.3—dimethylformamide (1:2)] and in 1 N NaOH in the presence of the dye Tetrazolium Blue (TB). Nitrotetrazolium Blue, which belongs to the same series of dyes, is widely used in the determination of $O_2^{\cdot -}$ [3]. The results show that on the oxidation of lignin in the presence of TB (30°C) absorption appeared in the spectrum in the 515-525 nm in the aqueous organic medium and at 555-560 nm in 1 N NaOH, due to the formation of a diformazan — the product of the reduction of TB (Fig. 1a). At 60°C and a partial pressure of O_2 of 1 atm, the absorption at 515-525 nm rapidly passed through a maximum in the course of the reaction (Fig. 1b), which may be connected with an instability of the diformazan under the given conditions.

To determine whether the formation of the diformazan took place on the interaction of TB with the oxygen radical anion we performed control experiments on the autooxidation of lignin in an aqueous organic medium using superoxide dismutase (SOD), which causes the specific inhibition of reactions with the participation of $O_2^{\cdot -}$ [3, 4]. The results of these experiments showed that the addition of SOD inhibited the increase in absorption at 515-525 nm (see Fig. 1), which confirmed the formation of the oxygen radical anion during the oxidation of lignin. In experiments on model lignin compounds it was shown that $O_2^{\cdot -}$ is formed rapidly in the oxidation of isoeugenol and slowly in the oxidation of vanillin.

Thus, the formation of the oxygen radical anion in the oxidation of lignin has been shown experimentally.

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ROLE OF SINGLET OXYGEN IN THE OXIDATION OF LIGNIN IN ALKALINE SOLUTIONS

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When lignin is oxidized in alkaline solutions, luminescence can be detected the spectra of which has a maxima at 470, 560, and 640 nm [1]. According to the literature [2, 3], the maximum at 560 nm is due to the radiative deactivation of carbonyl groups from the excited (triplet) state and the maximum at 640 nm reflects the passage of singlet oxygen, $^1O_2$, into the ground (triplet) state. Lymarev et al. [4] have assigned the radiation in the 500 and 630 nm regions to carbonyl-containing compounds and to singlet oxygen, respectively. However, no direct proofs have been given (apart from the spectral characteristics) of the formation of $^1O_2$ in the oxidation of lignin. The role of $^1O_2$ in the subsequent transformation of the lignin also remained unexplained.

It is known that furfuryl alcohol is a selective quenching agent for $^1O_2$ [5]. To prove the realization of processes connected with the formation of $^1O_2$ in the oxidation of lignin, we investigated the influence of furfuryl alcohol on the change in the intensity of chemiluminescence (I_{chl}) when Pepper lignin [6] was heated in 1 N NaOH solution in the temperature range from 40 to 100°C.

The results, which are presented in Fig. 1, show that I_{chl} and the total emission of light $\left(S = \int_{i=0}^{n} I_{\mathrm{chl}}\, d\tau_i\right)$ decreased with an increase in the concentration of added furfuryl alcohol. The dependence in the change in I_{chl} on the concentration of furfuryl alcohol is described by an equation analogous to the Stern—Volmer equation (Fig. 2). The activation energy

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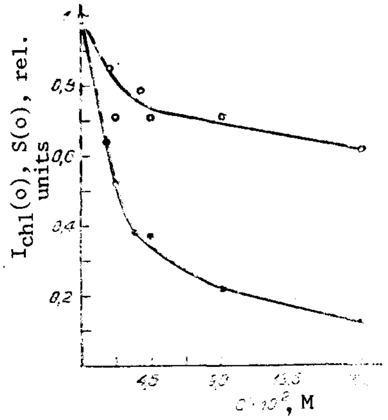

Fig. 1

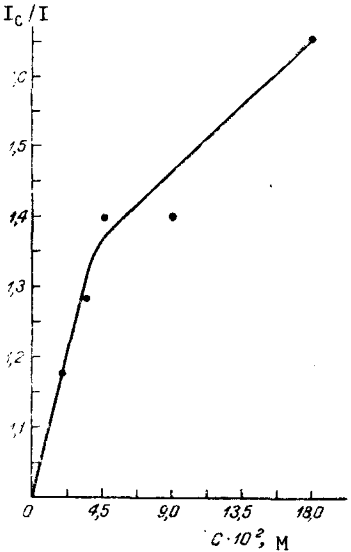

Fig. 2

Fig. 1. Change in Ichl and in the total amount of light (S) as functions of the concentration of furfuryl alcohol when lignin was heated. Experimental conditions: 100°C, 1 N solution of NaOH; lignin concentration 0.2 g/liter.

Fig. 2. Anamorphosis of the curve of the change in Ichl for lignin in the coordinates I_0/I vs. C.

of quenching is 9.6 J/mole and is in the range of activation energies for diffusion-controlled processes. It must be mentioned that at high concentrations of furfuryl alcohol oxygen is absorbed from the system.

Singlet oxygen can be formed as the result of the disproportionation of superoxide radical anions [7]:

$$2O_2^{\cdot} \xrightarrow{H_2O} H_2O_2 + {}^1O_2 + 2HO^- , \tag{1}$$

on the transfer of energy from electronically excited carbonyl groups present in the triplet state to an oxygen molecule [1]

$$RR_1^3 |C{=}O| + {}^3O_2 \rightarrow RR_1|C{=}O| + {}^1O_2, \tag{2}$$

or in the disproportionation of peroxide radicals [9]:

$$2RO_2^{\cdot} \rightarrow (1-n)\, RR_1|C{=}O| + nRR_1^3 |C{=}O| + ROH + {}^1O_2. \tag{3}$$

The formation of $^1O_2$ by reaction (1) is unlikely because of the low rate constant of the recombination of $O_2^{\dot{-}}$ [7]. Reaction (2), in essence, is the elementary act of reaction (3) when the migration of energy takes place from excited triplet states of carbonyl groups to molecular oxygen in a solvent cage.

Thus, the results presented confirm the hypothesis of the formation of singlet oxygen — probably by reaction (3) — when lignin is heated in alkaline solutions. The considerable decrease in the total amount of light emitted on the addition of furfuryl alcohol indicates the participation of singlet oxygen in free-radical transformations of lignin on heating.

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SYNTHESIS OF cis-DEC-5-en-1-ol ACETATE – ONE OF THE COMPONENTS OF THE SEX PHEROMONE OF *Agrotis segetum*

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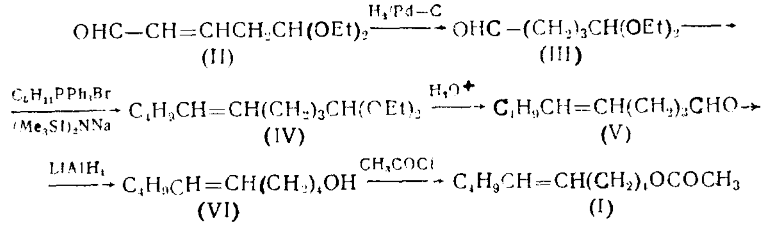
cis-Dec-5-en-1-ol acetate (I) is one of the main components of the pheromone of the turnip moth *Agrotis segetum (Lepidoptera Noctuidae)* that are responsible for the attraction of the males of this species under field conditions [1]. The traditional methods for the synthesis of the acetate (I) were based on the alkylation of lithium or sodium hexynylide with 2-(4-bromobutoxy)- or 2-(4-iodobutoxy)tetrahydropyran followed by the hydrogenation of the 2-(dec-5-enyloxy)tetrahydropyran to 2-(dec-5-enyloxy)tetrahydropyran and the conversion of the latter into (I).

We have performed a new synthesis of compound (I) starting from the readily available monoacetal of glutaconic aldehyde (II) [2]:



$$\underset{\text{(II)}}{OHC-CH{=}CHCH_2CH(OEt)_2} \xrightarrow{H_2/Pd-C} \underset{\text{(III)}}{OHC-(CH_2)_3CH(OEt)_2} \longrightarrow$$

$$\xrightarrow[(Me_3Si)_2NNa]{C_5H_{11}PPh_3Br} \underset{\text{(IV)}}{C_4H_9CH{=}CH(CH_2)_3CH(OEt)_2} \xrightarrow{H_3O^+} \underset{\text{(V)}}{C_4H_9CH{=}CH(CH_2)_3CHO} \rightarrow$$

$$\xrightarrow{LiAlH_4} \underset{\text{(VI)}}{C_4H_9CH{=}CH(CH_2)_4OH} \xrightarrow{CH_3COCl} \underset{\text{(I)}}{C_4H_9CH{=}CH(CH_2)_4OCOCH_3}$$

Compound (II) was hydrogenated in the presence of 5% palladium on carbon to the monoacetal of glutaraldehyde (III), bp 53-57°C/2 mm, n_D^{20} 1.4282. The reaction of the aldehyde (III) with amyltriphenylphosphonium bromide under the conditions described by Bestmann et al. [3] gave a 63% yield of the acetal of cis-dec-5-enal (IV), with bp 93-98°C/3 mm, n_D^{20} 1.3312. The hydrolysis of the acetal (IV) gave a 60% yield of cis-dec-5-enal (V), bp 60°C/1 mm, n_D^{20} 1.3332, which was reduced with lithium tetrahydroaluminate with a yield of 85% to cis-dec-5-en-1-ol (V), bp 75-76°C/1 mm, n_D^{20} 1.4512. The alcohol (VI) was converted by acetylation with acetyl chloride into the final acetate (I), bp 140°C/4 mm, n_D^{20} 1.4396.

It was established by gas-liquid chromatography on a column (0.4 mm × 4.5 m) containing 15% of OV-275 on Chromosorb P, 100-120 mesh, that 4% of the trans isomer of (I) was present.

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