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INFLUENCE OF THE POTENTIAL OF THE OXIDIZING
SYSTEM ON THE EXOTHERMIC STAGES IN THE
OXIDATION OF LIGNIN

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UDC 547.992.3:543.8

It has been shown that on the oxidation of soda lignin by the potassium ferri-ferrocyanide system thermal and luminous energy due to exothermic processes are evolved. The heat effect and also the total amount of light emitted are determined by the potential of the oxidizing system.

The development of the theory of soda and sulfate cooks and also of oxidative methods for the delignification and bleaching of lignocellulose materials raises the question of the investigation of redox processes in lignin. It is known [1] that lignin is a biopolymer of stereoirregular structure with various types of substitution of the phenylpropane structural units. The oxidation potential of model compounds of the structural unit of lignin are different and, consequently, it may be expected that the individual fragments in lignin [2] likewise differ in relation to their redox potentials. In actual fact, when using various oxidizing systems the oxidation processes take place differently. In view of the inhomogeneity and different properties of the individual fragments, it is general laws of the occurrence of redox processes in lignin that must be studied.

The oxidation of lignin is accompanied by the evolution of luminous energy (chemiluminescence), which shows the existence of exothermic or endothermic stages [3]. We have considered that the dependence of the evolution of thermal and luminous energy in the titration of an alkaline solution of soda lignin by a potassium ferri-ferrocyanide redox system on the potential of this system.

On titration, both thermal and luminous energy were evolved. The intensity of luminescence (I) in the process of titration passed through a maximum with a following fall (Fig. 1). The total amount of light emitted (S) and the dependence of the rise in temperature on the volume of titrant have sigmoid forms. The thermal effect of the process has been calculated from the results of calorimetry. With an increase in the potential of the oxidizing system from $E = 0.223$ V to $E = 0.300$ V the thermal effect, like the total amount of light emitted, rose to $\Delta H = 51.1$ kcal/nominal mole of lignin and $S = 2.17 \cdot 10^{-8}$ lm \cdot sec. With a rise in the potential of the oxidizing system they fell. The positive heat effect and the evolution of luminous energy indicate the existence of exothermic stages.

Siberian Scientific-Research Institute of Cellulose and Board, Bratsk. Translated from *Khimiya Prirodnikh Soedinenii*, No. 2, pp. 223-225, March-April, 1983. Original article submitted April 9, 1982.

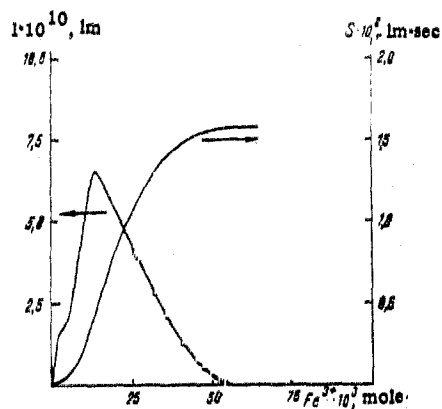


Fig. 1

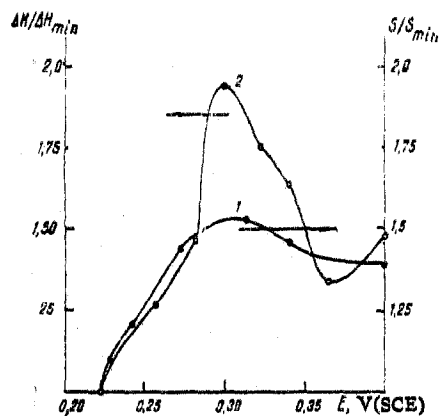


Fig. 2

Fig. 1. Dependence of the intensity of luminescence (I_{cl}) and of the total amount of light (S) on the amount of potassium ferricyanide.

Fig. 2. Dependences, brought to dimensionless form, of the heat effect (1) ($\Delta H/\Delta H_{min}$) and on the total amount of light (2) (S/S_{min}) on the potential of the oxidizing system.

In oxidation, they include recombination reactions and the disproportionation of the radical oxidation products [4]. Consequently, with a rise in the potential of the oxidizing system the concentration of radical products increases, i.e., phenolic elements with higher oxidation potentials take part in the oxidation process. A comparison with the results of cyclic voltammetry [2] shows that in the region of the maximum value of the heat effect and of the total amount of light there is an inverted peak of the reduction of the radical oxidation products ($E_{red} = 0.315$ V). In view of this, it may be assumed that the subsequent decrease in the heat effect and the emission of light is due to processes of two-electron oxidation to quinone methide structures, taking place with the consumption of energy, and also to degradation processes connected with the cleavage of $-C-C-$ and $-C-O-C-$ bonds in the lignin macromolecule which also proceed with the consumption of energy.

For a comparison with one another, the thermal effect and the total amount of light were brought to dimensionless forms. It can be seen from Fig. 2 that at a potential $E = 0.280$ V the dependences of the heat effect of the total amount of light on the potential of the oxidizing system change symbatically, and then with an increase in the potential the proportion of thermal processes rises. Consequently, in the range of potentials $E = 0.223-0.380$ V the evolution of thermal and luminous energy is determined by identical oxidation processes.

EXPERIMENTAL

For the calorimetric investigations we used an isothermal calorimeter consisting of a 250-cm³ Dewar vessel placed in a thermostat at a temperature of $25 \pm 0.1^\circ\text{C}$. The solution was stirred with a polyethylene stirrer. The solution of the titrant was thermostated in the same vessel in a polyethylene ampul. Temperatures were measured by means of a MT-64 semiconductor microthermistor of the Karmanov design with a resistance of 33 k Ω at $t = 20^\circ\text{C}$ and a temperature coefficient of 4.6%/deg. Recording was performed by bridge scheme with the output fed to a KSK-4 recording potentiometer. Before each series of measurements the calorimeter was calibrated in relation to current, for which purpose a heating element of low inertia was provided in the calorimetric vessel. Correction for heat exchange was performed graphically. The calorimeter was checked by titrating 150 ml of 0.01 M NaOH with a 0.2 M solution of HCl. When the correction for the heat of dissolution was taken into account, the value of the heat of neutralization differed from that given in the literature by 1.3% [5]. The method of thermometric titration was used. During an experiment, a $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox system with a definite potential relative to a silver chloride comparison electrode was added in portions to 150 ml of a solution of lignin in 1 M NaOH (lignin concentration 225 mg/liter). The ratio of titrant solution to lignin solution was 1:600, which

permitted foreign heat effects (heat of dilution, heat of mixing, etc.) to be eliminated to the maximum degree.

The chemiluminescence investigations were performed in a thermostated ($25 \pm 0.1^\circ\text{C}$) cell with a volume of 50 cm^3 . The titrant was added to the reaction medium which was stirred continuously with a glass stirrer with the aid of a micropump. The luminous energy evolved in the reaction was recorded by a FEU 84-2 multiplier cooled by a thermocouple of the "Selen" type. The hot junction of the thermocouple was cooled with running water at a temperature of 10°C .

The soda lignin was obtained by a three-hour cook of pine wood in an autoclave at 170°C . The alkaline solution obtained was acidified, and the lignin that precipitated was recovered by centrifugation. Then the lignin was washed to neutrality and was dried in a desiccator over phosphorus pentoxide.

SUMMARY

In the oxidation of lignin, the heat effect, and also the total amount of light emitted are determined by the potential of the oxidizing system.

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