CATALYSIS OF CHEMICAL REACTIONS BY METHODS ASSUMED TO BE SIMILAR TO ENZYMATIC METHODS COMMUNICATION 10.* OXIDATION IN THE PRESENCE OF A HOMOGENEOUS COMPLEX CATALYST COPPER (II) – POLY-4-VINYLPYRIDINE

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Polymer catalysts, as has been shown by the investigations of recent years, present new possibilities for increasing the rate and changing the specificity of the process [2]. It might be expected that the use of complexes based on polymers as homogeneous catalysts would be extremely promising, permitting a combination of the advantages of homogeneous low-molecular complex catalysts (saving of metal, relative ease of studying the mechanism of the process) with the possibilities provided by the polymer ligand (polyfunctional active center, weak interactions, conformational peculiarities).

In this work we produced and investigated the complex Cu(II) - poly-4-vinylpyridine [Cu(II) - PVP] for catalytic activity in an oxidation reaction. It is known that the complex of divalent copper with poly-vinylpicolinic acid [3] is active in the decomposition of hydrogen peroxide, while the complex with poly-L-histidine is active in the oxidation of a number of organic compounds [4].

<u>Production and Investigation of the Complex</u>. In the interaction of methanol solutions of $CuCl_2$ and poly-4-vinylpyridine, complex formation occurs, which is indicated by the appearance of a bright green color and absorption bands in the region of 262 and 435 nm. In an investigation of the catalytic activity of the solutions obtained at various N/Curatios, it was found that the greatest activity is achieved when the mole ratio of poly-4-vinylpyridine and copper is equal to 7-8 (Fig. 1). The maximum amount of the complex, as was shown by the method of isomolar series (λ_{max} 263 nm), is formed at ratios N/Cu = 7-8 (Fig. 2).

To isolate the complex, ether was added to the reaction mixture, after which a light green precipitate formed. It was filtered off, washed with methanol and ether, and dried; dec.temp.160-165°. Found: C 51.48; H 5.49; N 7.23; Cl 6.25; Cu 15.90%. Cu₃C₅₁H₇₄N₆O₉Cl₂. Calculated: C 52.00; H 6.30; N 7.15; Cl 6.02; Cu 16.20%.

An examination of the IR spectra of the isolated complex and of poly-4-vinylpyridine shows a shift of the bands characteristic of the valence C = C and C = N vibrations of the pyridine ring, as well as an intensification and redistribution of the intensities (in the region of 1400-1600 cm⁻¹ poly-4-vinylpyridine has bands 1432, 1469, 1565, 1586 cm⁻¹; the complex has bands 1432, 1474, 1578, 1590 cm⁻¹). In the region of the nonplanar deformational C - H vibrations of the ring, the initial polymer has a narrow band 748 cm⁻¹ and a weaker broad band 789 cm⁻¹. In the spectrum of the complex, the band 748 cm⁻¹ is shifted to 752 cm⁻¹; the intensity of the bands 752 and 789 cm⁻¹ increases sharply. The spectrum is also changed in the region of the deformational vibrations 1000-1200 cm⁻¹. New bands appear at 1029 and 1248 cm⁻¹, and the intensity of the band 1149 cm⁻¹ is also increased.

The conclusion of the formation of complexes in the interaction of polyvinylpyridine with chlorides of the metals Ti, Sn, Sb, Fe, and Al was drawn in [5] on the basis of an interpretation of the analogous IR spectra.

* For the preceding communication of this series, see [1].

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Fig. 1. Dependence of the rate of oxidation of 2,4,6-tri-tert-butylphenol on the mole ratio PVP/cupric chloride.

Fig. 2. Dependence of the concentration of the complex on the composition of the isomolar solution.

Fig. 3. Dependence of the rate of oxidation of the substrate on the pH. Cu(II) - PVP: 1) 3,4dihydroxycinnamic acid; 3) as corbic acid; 4) salicylic acid. A for 1-3: 10^{-4} , for 4: 10^{-5} . Cu(II) - pyridine: 2) 3,4-dihydroxycinnamic acid.

<u>Catalytic Activity of the Complex</u>. The catalytic activity of the complex was investigated in the oxidation of substituted phenols. As can be seen from Table 1, the complex Cu(II) – PVP is an active catalyst of the oxidation of substituted phenols. The reaction products are the corresponding 1,4-benzoquinones, as well as dihydroxydiphenyls. The rate of oxidation is a maximum if the reaction is conducted in methanol. The use of dimethyl sulfoxide or dimethylformamide as the solvent substantially lowers the rate of oxidation. Thus, 2,4,6-tri-tert-butylphenol (0.35 M) is oxidized in methanol in 30 min, in dimethyl sulfoxide in 240 min, while in dimethylformamide the oxidation proceeds very slowly and not to completion. The catalytic activity of the polymer complex obtained on the basis of copper chloride is higher than that of the analogous "monomer" complex (Table 2) [6]. The replacement of the chloride ion in the initial compound by nitrate, acetate, or acetylacetonate lowers the catalytic activity. On the basis of the data obtained it can be assumed that in the coordination sphere of copper of the polymer complex, one of the ligands is the methoxy group, which can readily be displaced by the substrate. By analogy with the conclusion drawn earlier for complexes of copper with pyridine [7], this structural peculiarity of the polymer complex is probably associated with the catalytic activity.

The Complex Cu(II) - PVP as a Bifunctional Catalyst. From the results obtained it is evident that not all the nitrogen of the polymer is coordinated with copper ions. Considering the ability of the nitrogen atom in pyridine for protonation, we might have attempted to use the complex Cu(II) - PVP as a bifunctional catalyst. The free nitrogen of pyridine in the complex has a positive charge, which depends on the pH of the solution. It seemed that with suitable selection of the substrates, we might have been able to use the peculiarity of the polymer complex to increase the ability of the substrate to form complexes with the catalyst close to the active center (Schemes 1-4)

$$[\mathbf{L} - \mathbf{Cu}(\mathbf{II}) - \mathbf{L}(\mathbf{N})]_n + \mathbf{HCI} \rightleftharpoons [\mathbf{L} - \mathbf{Cu}(\mathbf{II}) - \mathbf{L}(\mathbf{N})^+ \mathbf{H}]_n + \mathbf{CI}^-$$
(1)

$$XAH \rightleftharpoons XA^- + H^+$$

$$[\mathbf{L}-\mathbf{Cu} (\mathbf{II})-\mathbf{L}(\mathbf{N})+\mathbf{H}]_n \rightleftharpoons [\mathbf{L}-\mathbf{Cu} (\mathbf{II})-\mathbf{L} (\mathbf{N})+\mathbf{H}]_n$$
(3)*

(2)

$$H^+ + Cl^- \rightleftharpoons HCl \qquad \qquad XA^- \qquad (4)$$

Here $[L - Cu(II) - L(N)]_n$ is the polymer complex catalyst (L is a ligand bonded to copper; L(N) is the vinylpyridine fragment with uncoordinated nitrogen); XAH is the substrate (X is the group to be oxidized; AH is a substituent containing a labile hydrogen atom).

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For the investigation we selected 3,4-dihydroxycinnamic, salicylic, and ascorbic acids, as well as 2,5-dihydroxyacetophenone, which possess a substantial dipole moment. 2,4,6-Tri-tert-butylphenol was selected as the neutral substrate. We considered paraphenylenediamine as an electropositive substrate.

*As in Russian original - Consultants Bureau.

Initial compound	Oxidation products	Yield, %	
2,4,6-Tri-tert-butylphenol	2,6-Di-tert-butylbenzoquinone	95	
2,4-Di-tert-butylphenol	2,2'-Dihydroxy-3,3', 5, 5'-tetra-tert-butyldiphenyl	70	
2,6-Dimethoxyphenol	1,1',2,2', - Tetramethoxybenzoquinone	95	
tert-Butylhydroquinone	tert-Butylbenzoquinone	90	
2,6-Di-tert-butyl-4-methylphenol	2,2',5,5'-Tetra-tert-butyl-1,1'-dihydroxydiphenyl-		
	ethane	30-40	
	2,2',5,5'-Tetra-tert-butylstilbenequinone	25	
Hydroquinone	Benzoquinone		

TABLE 1.	Initial F	Phenols and	Their	Oxidation	Products	on the	Catalyst	Cu (II)	– PVP
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TABLE 2. Catalytic Activity of Copper Ions of Various Complexes of Cu(II) in the Oxidation of 2,4,6-Tri-tert-butylphenol

	Rate of absorption of oxygen-10 ⁻³ , mole/liter-min					
Copper salt	free Cu ²⁺ ions	Cu ²⁺ + Py	Cu ²⁺ + PVP			
CuCl ₂ ·2H ₂ O Cu(NO ₃) ₂ ·6H ₂ O Cu (CH ₃ COO) ₂ · H ₂ O Cu (acac) ₂	6.4 Practically not oxidized 0.93 Practically not oxidized	4,2 6,65 13,0	17,4 2,4 3,7			

<u>Note</u>: 25°; [copper salt] = $2 \cdot 10^{-2}$ M; [substrate] = 0.35 M.

From Fig. 3 (curve 1) it is evident that the rate of oxidation of 3,4-dihydroxycinnamic acid in the presence of the complex Cu(II) - PVP at first increases with increasing pH of the solution, reaches a maximum, and then drops. At the same time, on the "monomeric" copper-pyridine complex, the rate of oxidation increases with increasing pH, but then remains constant (curve 2). The presence of a maximum in the oxidation of 3,4-dihydroxycinnamic acid on the polymer complex can evidently be explained by the fact that when the acidity of the solution is increased; hydrogen ions protonate the free nitrogen of pyridine, and as a result of the electrostatic interaction between the polyelectrolyte and the anionic substrate, the concentration of the latter increases close to the active center, and the rate of oxida-

tion increases. After a definite pH has been reached, an excess of protons appears, which prevents dissociation of the acid and thereby reduces the electrostatic effect. In the oxidation of ascorbic acid on the polymer complex, a maximum was also observed, lying at pH 4.2 (curve 3). The results obtained in the oxidation of salicylic acid show that the maximum of the reaction rate is reached at pH 3 (curve 4).

Figure 4 depicts the dependence of the rate of oxidation of 2,5-dihydroxyacetophenone on the pH. It is evident that when the pH is lowered, the rate of oxidation increases, passes through a maximum, and then drops. This can probably be explained by the fact that in polar media the dipole moment of the substance increases [8]. With increasing dipole moment, the possibility is increased of electrostatic interaction between the polymer complex protonated by the nitrogen of pyridine and the carbonyl group of 2,5dihydroxyacetophenone. A substantial decrease in the pH leads to a decrease in the reaction rate on account of strong interaction of the protons with the carbonyl group.

As the neutral substrate we used 2,4,6-tri-tert-butylphenol. From Fig. 5 (curve 1) it is evident that this phenol is oxidized at considerably higher pH than negatively charged substrates. The rate of oxidation at first increases with increasing pH, then remains constant. In the case of a positively charged substrate (paraphenylenediamine), the rate of oxidation drops sharply when the acidity of the solution is increased (curve 2). This is evidently explained by the electrostatic repulsion of the like-charged polyelectrolyte and substrate.

An investigation of the kinetics of the reaction at constant pH also indicates a difference between negatively charged and neutral substrates. The oxidation of ascorbic acid, as can be seen from Fig. 6 (curve 1), at relatively low concentrations obeys a first-order equation with respect to the substrate. When the concentration of the substrate is increased, beginning with a substrate/catalyst ratio of 30, the initial rates approach a maximum value, i.e., the order of the reaction with respect to the substrate changes from first to zero. There is a linear relationship between the values of the reciprocal rates and the reciprocal concentrations. It may be assumed that as a result of electrostatic interaction between the polyelectrolyte and ions of ascorbic acid, the concentration of the latter close to the polymer increases with increasing amount of acid, and the rate of oxidation increases. When a certain ascorbic acid concentration is reached, all the active centers of the polymer complex are saturated by the substrate, and a further increase in its concentration has no significant influence on the rate of oxidation. Consequently, the oxidation of ascorbic acid under these conditions obeys the Michaelis – Menten equation and proceeds with the formation of an intermediate complex.



Fig. 4. Dependence of the rate of oxidation of 2,5-dihydroxyacetophenone on the pH.

Fig. 5. Influence of pH of the solution on the rate of oxidation: 1) 2,4,6-tritert-butylphenol; 2) paraphenylenediamine. A for 1: 10^{-3} , for 2: 10^{-4} .

Fig. 6. Dependence of the rate of oxidation on the substrate concentration: 1) ascorbic acid; 2) 2,4,6-tri-tert-butylphenol.

Curve 2 of Fig. 6 shows that the rate of absorption of oxygen is a linear function of the amount of 2,4,6-tri-tert-butylphenol. Evidently such a dependence is associated with the absence of an electrostatic interaction between the substrate and the protonated nitrogen of the complex. In view of this, the concentration of substituted phenol close to the active centers of the polymer complex will depend to a substantial degree on the concentration of phenol in the entire volume of the reaction medium.

EXPERIMENTAL

The initial phenols and 3,4-dihydroxycinnamic acid were produced according to the methods of [9-12]. Brand "B" hydroquinone was recrystallized twice from water. Oxidation was conducted with molecular oxygen in a thermostatically controlled vessel with shaking at 25° and atmospheric pressure. The reaction rate was measured according to the absorption of oxygen from a gas burette. The pH of the solutions was measured on a pH-meter of the LPU-01 type; the IR spectra were taken on an IR-10 spectrometer; spectrophotometric measurements were conducted on SF-4 and SF-10 spectrophotometers.

The oxidation products of 2,4,6-tri-tert-butylphenol, 2,4-di-tert-butylphenol, 2,6-di-tert-butyl-4methylphenol, and tert-butylhydroquinone were isolated by acidification of the reaction mixture with dilute HCl and extraction of the solution with ether. The ether extracts were dried and the ether distilled off. The oxidation product of 2,6-dimethoxyphenol precipitated; it was filtered off, washed with methanol, and dried.

The isolated products were identified according to the melting points. A mixed sample with known substances synthesized according to the methods of [13-15] showed no depression of the melting point.

CONCLUSIONS

1. A homogeneous polymer complex catalyst based on poly-4-vinylpyridine and cupric chloride, active in the oxidation of substituted phenols, was produced.

2. In the oxidation of 3,4-dihydroxycinnamic, ascorbic, and salicylic acids and 2,5-dihydroxyacetophenone, the reaction rate passes through a maximum when the acidity of the medium is varied.

3. The presence of a maximum is evidently associated with the formation of a complex between the substrates and the catalyst on account of an electrostatic interaction. The polymer complex functions as a bifunctional catalyst in the indicated cases.

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