SCHIFF'S BASES IN THE POLYMER MATRIX.
COMMUNICATION 2. STRUCTURE AND CATALYTIC PROPERTIES OF Cu(II) COMPLEXES WITH AROMATIC AND HETEROCYCLIC AZOMETHINES IN THE STYRENE–DIVINYLBENZENE COPOLYMER IN OXIDATION OF 2,3,6-TRIMETHYLPHENOL

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One of the best studied systems used for oxidation of phenols is Fenton's reagent (H_2O_2 + Fe^{2+}), whose mechanism of action is due to the formation of OH radicals. It has been found that decomposition of H_2O_2 in the presence of Fe^{2+} and Cu(II) ions is similar in character [1]. For this reason, it was interesting to study the catalytic activity and selectivity of complexes of Cu(II) with Schiff's bases attached to the polymer matrix of the styrene–divinylbenzene copolymer [2] and the character of the products and changes in the structure of the catalytic sites to select between the molecular ion and radical ion mechanisms of the reaction. The use of this type of catalyst is more promising with respect to separation of the target products and the possibility of repeated use of the catalyst.

The catalytic activity of complexes of Cu(II) with polymeric Schiff's bases prepared by the reaction of aminomethylated copolymer of styrene with 8% divinylbenzene (Ps) with aromatic and heterocyclic aldehydes (salicylaldehyde, pyridine-2-aldehyde, furfural, benzothiazole-2-, benzoxazole-2-, and benzimidazole-2-aldehydes) was studied in the reaction of liquid-phase oxidation of 2,3,6-trimethylphenol (TMP) by hydrogen peroxide. It was previously [2] shown by EPR that in the case of almost quantative formation of Schiff's bases in the polymer matrix of an ion-exchanger, Cu(II) complexes were formed with the participation of two residues of the Schiff's bases, while in the case of the incomplete occurrence of this reaction (for example, with pyridine-2-aldehyde), a mixed complex involving one residue of Schiff's bases and the unreacted NH_2 groups is formed in the ion-exchanger phase. The incomplete occurrence of the reaction with respect to the primary NH_2 groups of the AN-20 anion-exchanger is also characteristic of carbonyl compounds of the benzazole series, which suggests the formation of mixed Cu(II) complexes in the resin phase. The parameters of the EPR spectra of all of the samples are reported in Table 1. The same parameters of the EPR signals of Cu(II) in samples (IV) and (V) indicate the similar structure of the Cu complexes in these resins. The first complex ($g_\parallel = 2.228$, $A_\parallel = 168\cdot10^{-4}$ T) apparently corresponds to Cu ions surrounded by four amino groups [3]. The second set of parameters ($g_\parallel = 2.279$ and $A_\parallel = 156\cdot10^{-4}$ T) is assigned to a copper diamine complex [4]. This analysis permitted indicating in Table 1 the reaction of Cu(II) with the nitrogen atoms at the double bond for samples (IV) and (V).

Two Cu(II) complexes are also formed in sample (VI). The first is similar to the complex formed in the ion-exchanger (II) and is due to Cu ions bound with two functional groups in the resin which manifest bidentate properties due to the nitrogen and oxygen atoms. Judging by the parameters, the second complex can be assigned to either a complex of Cu with one bidentate functional group or Cu in a purely oxygen environment. Liquid-phase oxidation of TMP by H_2O_2 in the presence of different Cu(II) compounds with polymeric Schiff's bases was conducted in the conditions reported in Table 2. The catalytic activity of the samples was evaluated by the conversion of TMP and the selectivity of formation of 2,3,5-trimethylbenzoquinone (TMBQ). The data obtained permit analyzing the dependence of the catalytic properties of the polymeric Cu(II) complexes on their structure. The best results were obtained for the samples containing Schiff's bases of salicylaldehyde and benzoxazole-2-

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TABLE 1. Parameters of the EPR Spectra of Complexes of Cu(II) Attached in the Polymer Matrix

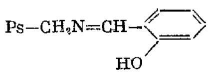
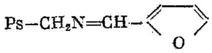
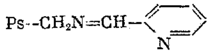
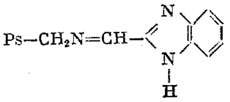
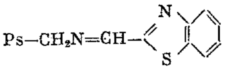
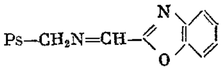
Compound	Ligand	$g_{\parallel} \pm 0{,}003$ $(A_{\parallel} \pm 5)\cdot 10^4$, T			
		before reaction		after reaction	
(I)		2,236	166	2,31	150
(II)		2,248	161	2,276	165
(III)		2,251	167	2,314	150
(IV)		2,228 2,279	168 156	2,308 2,355	156 136
(V)		2,228 2,279	168 156	2,252 2,280	170 160
(VI)		2,249 2,331	165 148	2,274 2,334	162 152

TABLE 2. Catalytic Activity of Complexes of Cu(II) with Polymeric Schiff's Bases in the Reaction of Oxidation of TMP by H_2O_2 at 50°C

Sample	TMP:solvent:H_2O_2: Cu(II) molar ratio	Concentration of Cu(II), mmole/g	Reaction time, h	Solvent	Conversion for TMP, %	Selectivity for TMP, %
(I)	1 : 350 : 50 : 0,05	0,37	3	Acetone	55,0	22,3
(I)	1 : 690 : 104 : 0,05	0,38	3	»	92,3	28,8
(I)	1 : 690 : 104 : 0,05	0,38	1	»	63,4	14,4
(I)	1 : 350 : 104 : 0,01	0,16	3	Acetonitrile	65,8	17,0
(II)	1 : 690 : 104 : 0,05	0,46	3	Acetone	45,9	15,7
(III)	1 : 536 : 312 : 0,06	0,90	3	»	96,7	2,3
(IV)	1 : 336 : 312 : 0,02	0,34	2	»	98,4	0,4
(IV)	1 : 530 : 208 : 0,02	0,34	1	Acetonitrile	94,6	3,7
(V)	1 : 690 : 104 : 0,03	0,40	3	Acetone	75,0	14,9
(VI)	1 : 690 : 104 : 0,01	0,20	3	»	56,8	25,4

aldehyde as the polymeric ligands; the complexes of Cu with Schiff's bases prepared from furanaldehyde and pyridine-2-, benzothiazole-2-, and benzimidazole-2-aldehydes were the least effective. One of the products of the reaction, the product of oxidative association of 2,2',3,3',5,5'-hexamethyl-4,4'-dioxyphenyl, was synthesized according to [5] and identified in the products of oxidation. The low selectivity of formation of TMBQ could be due to oxidative cleavage of the quinoid ring. A sample of catalyst containing salicylidene groups as the ligands was selected for studying the effect of the parameters of the reaction on oxidation of TMP by H_2O_2. The results of the dependence of conversion of TMP (a) and the selectivity of formation of TMBQ (b) on the temperature, concentration of Cu(II) ions in the ion-exchanger phase, and reaction time are shown in Fig. 1. The optimum conditions of the reaction of oxidation of TMP into TMBQ are: 0.15-0.45 mmole/g concentration of Cu(II) ions in the ion-exchanger phase, temperature of 40-50°C, and reaction time of 1-3 h. The EPR studies showed that the Cu complexes in the ion-exchangers (see Table 1) undergo certain changes as a result of the catalytic reaction. Regardless of the type of ionogenic group and structure of the starting complex, a set of two EPR signals with the same parameters which differed in the samples with respect to a different ratio of the intensities was observed in all of the samples studied. The changes which took place in the values of the parameters of the EPR spectra were interpreted as a successive decrease in the number of nitrogen atoms in the first coordination sphere of the Cu ions and their substitution by oxygen. If the signal with parameters ($g_{\parallel} = 2.310$ and $A_{\parallel} = 150\cdot 10^{-4}$ T) corresponds [6, 7]

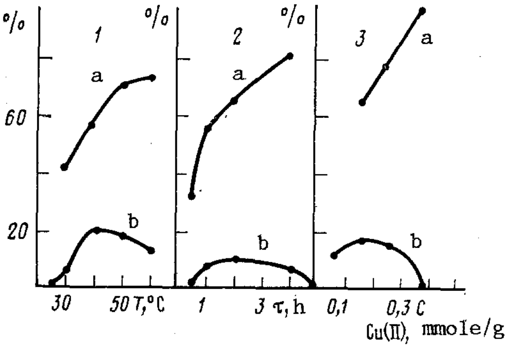


Fig. 1. Dependence of conversion of TMP (a) and selectivity of formation of TMBQ (b) in sample (I) on the parameters of the reaction: 1) temperature (TMP:acetone:H_2O_2:Cu(II) molar ratio = 1:690:104:0.05), τ = 3 h; 2) reaction time (same molar ratio, 40°C); 3) concentration of Cu(II) in the sample (TMP:acetonitrile:H_2O_2 molar ratio = 1:350:104; 50°C, 0.05 g weighed portion of sample, τ = 3 h).

to coordination of one nitrogen atom by the Cu ion, then the signal with parameters ($g_{\parallel} = 2{,}353$ and $A_{\parallel} = 132 \cdot 10^{-4}$ T) belongs to a Cu complex with a purely oxygen environment [8]. This process is a function of both the time of work of the catalyst and the amount of H_2O_2 added to the reaction mass. The values of the parameters of the EPR spectra of the Cu(II) complex of sample I with a 0.38 mmole/g concentration of the metal changed from $g_{\parallel}{}^1 = 2{,}236$ and $A_{\parallel}{}^1 = 166 \cdot 10^{-4}$ T through $g_{\parallel}{}^2 = 2{,}310$ and $A_{\parallel}{}^2 = 150 \cdot 10^{-4}$ T to $g_{\parallel}{}^3 = 2{,}354$ and $A_{\parallel}{}^3 = 131 \cdot 10^{-4}$ T after catalytic oxidation of TMP with the same volume of 90% H_2O_2 in EtOH solution (see Table 1).

Note that if the ion-exchanger complex is most active in the catalytic process studied (almost quantitative conversion of TMP), its rearrangement takes place during catalysis and signals whose parameters are similar to those observed for ion-exchanger (I) are found in the EPR spectrum. If the ion-exchange catalyst is less active, the Cu complex changes to a significantly smaller degree. The appearance of the same Cu complexes as a result of the catalytic reaction regardless of the type of functional group in the starting samples of catalysts can be attributed to oxidation of the matrix of the catalysts with cleavage of part of the attached Schiff's bases.

The probability of such processes during catalytic oxidation of substituted phenols by H_2O_2 is indicated by the changes in the IR spectra of the catalysts before and after the reaction. The disappearance of the absorption band of the metal-coordinated C=N bond at 1620 cm^{-1} and the appearance of a broad absorption band in the 1650-1700 cm^{-1} region, assigned to symmetric and antisymmetric vibrations of COOH groups, are observed in the complex of Cu(II) with salicylidene groups.

In conditions considered optimum for oxidation, treatment of the catalyst with H_2O_2 in the absence of substituted phenols results in the same changes in the structure of the copper complexes. In addition, treatment of the starting samples of the ion-exchangers with H_2O_2 and subsequent sorption of Cu ions on them demonstrated the formation of the same oxygen-enriched Cu complexes. The set of these data shows that oxidation of the matrix of the ion-exchanger, accompanied by cleavage of functional groups, takes place parallel to the reaction of oxidation of TMP. The presence of products of an acid type in the reaction mixture permits hypothesizing a radical ion mechanism of catalytic oxidation of TMP.

EXPERIMENTAL

The IR spectra were made on an UR-20 spectrophotometer in vaseline lubricant. The EPR spectra of the polymer samples were recorded at ~20°C in the x-range on a RE-1307 radiospectrometer. Benzoxazole-2-aldehyde was prepared by oxidation of 2-methylbenzoxazole with SeO_2 according to [9]. Benzothiazol-2-aldehyde was also synthesized by oxidation of 2-methylbenzothiazole with SeO_2 [10]. Benzimidazol-2-aldehyde was prepared by condensation of tartaric acid and o-phenylenediamine with subsequent oxidation of the 2,2-(dioxyethane)dibenzimidazole formed with KIO_4 [11].

Incorporation of azomethine groups in the insoluble matrix was conducted by the reaction of a four-fold excess of a carbonyl compound of the polymer with primary NH_2 groups for 8 h at ∿20°C in anhydrous MeOH. The reaction with benzimidazol-2-aldehyde was conducted in DMF.

Elementary analysis of the AN-20 anion-exchanger: C 78.5, H 7.1, N 4.5%. After reactions with benzoxazole-2-aldehyde, found: C 79.1; H 7.5, N 5.8%. Calculated: C 77.27, H 5.69, N 6.32%. With benzothiazol-2-aldehyde, found: C 73.9, H 6.0, N 5.9, S 4.0%. Calculated: C 74.58, H 5.50, N 6.10, S 6.87%. With benzimidazole-2-aldehyde, found: C 78.1, H 7.8, N 5.9%. Calculated: C 77.10, H 6.36, N 9.46%. In the samples studied, the absorption band of the azomethine bond appeared at 1634, 1641, and 1648 cm^{-1}. The exchange capacity of the synthesized Schiff's polybases for Cu(II) ions was determined in static conditions based on the difference in the concentrations of the metal ions before contact with the ion-exchanger in the equilibrium state.

TMP was oxidized in a thermostatted three-neck flask while stirring. H_2O_2 was added by drops to determined molar ratio of TMP and solvent in the presence of the catalyst. As the reaction time elapsed, 50 ml of H_2O was added, the catalyst was filtered off, and the product of oxidation was analyzed by GLC on a Khrom-5 chromatograph with a flame-ionization detector in the temperature programming mode from 120 to 230°C on Chromaton N-AW-DMCS with 10% Lucoprene G-1000. The internal standard was 1,3,5-trimethylbenzene. The coefficient of variation was 5%.

CONCLUSIONS

1. Complexes of Cu(II) with polymeric Schiff's bases prepared by the reaction of the AN-20 ion-exchanger with aromatic and heterocyclic aldehydes can be used as heterogeneous catalysts of oxidation of 2,3,6-trimethylphenol by hydrogen peroxide.

2. Based on an analysis of the data from the IR and EPR spectra, a conclusion was drawn concerning the character of the change in the catalytic centers during the oxidation reaction.

LITERATURE CITED

1. A. Ya. Sychev, Redox Catalysis of Metal Complexes [in Russian], Shtinnitsa, Kishinev (1976), p. 110.
2. L. A. Petrov, S. Yu. Men'shikov, I. P. Koalenko, et al., Proceedings of the 15th All-Union Tschugaeff Conference on the Chemistry of Complexes [in Russian], Kiev (1985), p. 17.
3. I. N. Marov, L. S. Molochnikov, E. N. Kazantsev, et al., Zh. Neorg. Khim., 21, 483 (1976).
4. L. S. Molochnikov, G. P. Vishnevskaya, R. Sh. Safin, et al., Koord. Khim., 10, 926 (1984).
5. French Patent No. 2454431 (1979); Ref. Zh. Khim., 4N114P (1982).
6. G. P. Vishnevskaya, L. S. Molochnikov, R. Sh. Safin, et al., Koord. Khim., 8, 741 (1982).
7. A. I. Kokorin, V. V. Berentsveig, V. D. Kopylova, and E. L. Frumkina, Kinet. Katal., 24, 181 (1983).
8. G. P. Vishnevskaya, R. Sh. Safin, I. N. Lipunov, and E. I. Kazantsev, Teor. Éksp. Khim., 11, 651 (1985).
9. A. M. Osman, M. S. K. Youssef, and Z. H. Khalil, J. Appl. Chem. Biotechnol., 26, 762 (1976).
10. V. M. Zubarovskii, Dokl. Akad. Nauk SSSR, 87, 760 (1952).
11. B. H. Chase and J. M. Evans, J. Chem. Soc., 4829 (1964).