Structural changes in copper(II) complexes with polyamine anion exchangers in the course of liquid-phase oxidation

A. I. Kokorin

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: 007 (095) 938 2156

In the course of liquid-phase catalytic oxidation, the coordination spheres and three-dimensional structures of the Cu^{II} complexes with various polyamine anion exchangers are changed. The main regularities of these changes were studied by ESR and IR spectroscopy. It was demonstrated that these transformations occur stepwise, which is associated with successive oxidation of the coordinated amino groups of the polymer-metal complexes in the reactions with the participation of molecular oxygen and hydrogen peroxide. The possible mechanisms of transformation of the metal complexes is discussed.

Key words: copper, anion exchangers, complexes; structure; ESR spectra; oxidation reactions, catalysis.

Polymer-metal complexes are catalysts for various liquid-phase oxidation reactions. Many of these reactions proceed by a radical-chain mechanism.[1–3] The characteristic feature of most oxidation reactions is the stage of reversible change in the valence of the coordinated metal ion. Generally, the coordination spheres of the complexes, which contain metal atoms in different oxidation states, differ substantially in composition and structure. In the case of polymer-metal complexes, rearrangements of the complexes may be sterically hindered due to the macromolecular nature of the ligands. This leads to the appearance of a number of structures that adopt thermodynamically unfavorable conformations and exhibit enhanced reactivities. This fact along with the formation of highly active free (or coordinated) radicals in the course of oxidation may cause changes in the structure of the polymer-metal complexes and their catalytic properties.

With the aim of elucidating the main regularities and characteristic features of the changes in composition and structure of the polymer-metal complexes in the course of redox catalytic processes, we chose liquid-phase oxidation reactions of three types: oxidation of sulfur-containing compounds, oxidation of hydrocarbons, and decomposition of hydrogen peroxide:

$$RH + O_2 \longrightarrow \text{Products}, \qquad (1)$$

$$RSH + O_2 \longrightarrow RSSR + H_2O, \qquad (2)$$

$$H_2O_2 \longrightarrow H_2O + O_2 \qquad (3)$$

In this work, we did not seek to elucidate the mechanism of these reactions in detail. Most attention was concentrated on the structural changes in the polymer-metal complexes and their relationship with the catalytic activity.

Experimental

We used helium (AN-31) and macroporous low-basicity anion exchangers AN-521, AN-511, AN-221, and EDE-10p, which contain primary and secondary amino groups.[4] Procedures for the purification of anion exchangers from inorganic and low-molecular-weight impurities, preparation of deprotonated and partially protonated forms of anion exchangers, synthesis of the copper-containing complexes, determination of their compositions, and kinetic studies have been reported previously in detail.[6–8] It has been established that the above-mentioned anion exchangers do not exhibit catalytic activity in the absence of Cu^{II}.[4,6–8]

We used cumene $PhCHMe_2$ and 1-butanethiol C_4H_9SH as typical representatives of hydrocarbons and sulfur-containing compounds, respectively.

The ESR spectra were recorded on Varian E-4 and EPR-V radiospectrometers (3-cm range) in the Institute of Chemical Physics of the Russian Academy of Sciences at 298 and 77 K using 4 mm-diameter thin-walled quartz tubes. Precise calibration of the magnetic field was carried out using diphenylpicrylhydrazyl (g = 2.0036) and Mn^{2+} ions in the MgO matrix as the standards. The principal values of the g tensor, $g_{\parallel}$ and $g_{\perp}$, and the constants of the hyperfine interaction between the unpaired electron and the nucleus of the copper ion $A_{\parallel}$ were determined from the ESR spectra using the known formulas.[5] The procedure for the determination of the average local concentration of copper ions in the polymer-metal complexes, $[Cu]_{loc}$, which characterizes the true concentration of the copper complexes in the regions of their localization in the polymeric matrix, has been reported previously in detail[9,10] (the value of $[Cu]_{loc}$ was measured in cm^{-3} or in mol L^{-1} [10]).

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* Presented at the First Moscow Workshop on Highly Organized Catalytic Systems (June 19, 1996).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1824—1829, October, 1997.

The absorption spectra of solutions were measured on a Specord UV-Vis spectrophotometer. The IR spectra of the polymer-metal complexes were recorded on UR-20 and Specord 75-IR spectrometers. The ESR spectra of the polymer-metal complexes obtained after oxidation were recorded using samples of the catalysts, which were preliminarily dried in air at ~20 °C for 2 h without additional purification from the reaction products. The polymer-metal complexes studied by IR spectroscopy were washed three times (each for 30 min) with benzene, dried *in vacuo* with the use of a water jet pump, and prepared as KBr pellets.

Results and Discussion

Oxidation of hydrocarbons. Studies of the catalytic properties of the copper-containing polymer-metal complexes demonstrated that the activities of many anion-exchange catalysts decreased when these catalysts were used repeatedly or over a long period. For example, when the polymer-metal complex Cu(AN-521) was used in the oxidation of cumene by oxygen during 8 and 15 h, the catalytic activity decreased tenfold and by a factor of more than 50, respectively (Fig. 1). Analogous changes were observed for AN-221 and AN-511.[8] Granules of the catalyst changed color from blue to greenish, which is indicative of the change in the structure of the copper complexes. The initial polymer-metal complex is a slightly elongated octahedron with four N atoms in the equatorial plane and two H_2O molecules in the axial positions. Substantial changes are observed in the ESR spectra of the catalysts used during several hours in a reactor, that is, the amplitudes of the spectral lines belonging to the $Cu(N)_4$ complex and the amplitude of the singlet line, which characterizes associates with a high local concentration of Cu^{II}, decrease.[8] Simultaneously, the lines corresponding to isolated complexes of alternative compositions appear. The measured values of $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}$ are given in Table 1.

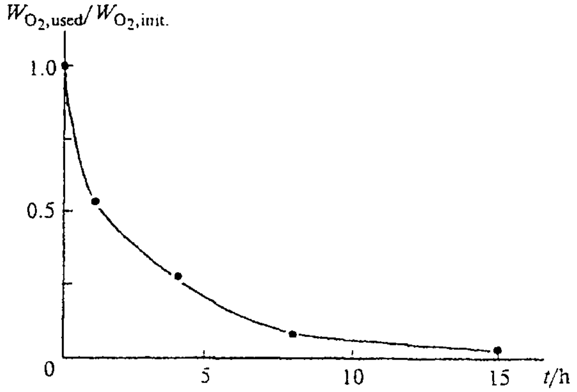


Fig. 1. Dependence of the activity of the Cu(AN-521) catalyst on the time of use in the liquid-phase oxidation of cumene by oxygen at 363 K.

The chemical processes leading to the changes in the coordination centers in the course of catalytic liquid-

Table 1. Changes in the parameters of the spin-Hamiltonians of the Cu^{II} complexes with anion exchangers in the course of catalytic oxidation

Reaction	Anion exchanger	Initial complex	Before the reaction		After the reaction		Reference
			$A_{\parallel}$	$g_{\parallel}$	$A_{\parallel}$[a]	$g_{\parallel}$[b]	
			mT				
Cumene + O_2	AN-521	$Cu(N)_4$	18.0	2.214	15.7	2.295	
TMP[c] + H_2O_2	AN-221	$Cu(N)_4$	18.4	2.207	19.0	2.226	20
TMP[c] + H_2O_2					14.8	2.263	
TMP[c] + H_2O_2	AN-84	$Cu(N)_4$	16.7	2.203	17.3	2.228	
TMP[c] + H_2O_2	AN-20	$Cu(N)_2$	16.2	2.266	15.6	2.316	
TMP[c] + H_2O_2	AN-21	$Cu(N)_2$	16.7	2.265	16.5	2.307	
n-Dodecane + O_2	AN-31	$Cu(N)_4$	18.0	2.210	16.1[d]	2.228[d]	16
					15.3[e]	2.304[e]	
	AN-31n	$Cu(N)_4$	16.3	2.205	16.7[d]	2.233[d]	
					15.0[e]	2.309[e]	
C_4H_9SH + O_2	AN-221	$Cu(N)_4$	17.5	2.210	15.0	2.27	13
Na_2S + O_2	EDE-10p	$Cu(N)_4$	17.9	2.208			14
LMW[f]	AN-511	$Cu(N)_4$	18.4	2.220			21
LMW[f]	AN-221	$Cu(N)_4$	19.2	2.202			21
LMW[f]	—	CuL[g]	16.3	2.291			8
LMW[f]	—	CuL_2[g]	18.7	2.215			8
LMW[f]	—	$Cu(Gly)^+$[h]	15.6	2.319			18
LMW[f]	—	$Cu(Gly)_2$[h]	17.4	2.263			18

[a] ±0.3. [b] ±0.005. [c] TMP — 2,3,6-Trimethylphenol. [d] After 6 h. [e] After 12 h. [f] LMW — low-molecular weight complex. [g] L — 1,2-Diethylenediamine. [h] Gly — Glycine.

phase oxidation of cumene are confirmed by the data of IR spectroscopy. The IR spectra of the "exhausted" catalyst have new absorption bands in the 1800—800 cm^{-1} region. The bands at 1320 and 910 cm^{-1} correspond to the deformation vibrations of the hydroxyl groups.[11] In the 3700—3100 cm^{-1} region, the band corresponding to the stretching vibrations of the N—H bonds of the imino groups is substantially broadened, apparently, due to the appearance of groups bonded to the imino groups through hydrogen bonds. The bands typical of oxides of aliphatic amines and carbonyl compounds are present in the regions of 965 and 1730 cm^{-1}, respectively.[11,12] Therefore, in the course of oxidation of cumene by O_2, the hydrocarbon matrix of the anion exchanger as well as the ionogenic amino groups are oxidized.

The data of elemental analysis demonstrated[8] that when the catalyst was used over a long period (longer than 10 h), up to 70% of copper atoms, which were present initially in AN-521, were removed from the anion-exchange matrix. The above-mentioned facts account for the rapid decrease in the activity of the catalysts based on the polyamine anion exchangers because surface complexes, which comprise a relatively small part of the total number of the polymer-metal complexes in the anion exchanger, become passive first. It was demonstrated that the relative concentration of $Cu(N)_4$ complexes in AN-521 correlates with the decrease in the activity of this catalyst with time.[8]

To elucidate the possibility of the deep rearrangement of the polymer-metal complexes in the course of oxidation, we studied the changes in the structures of the ethylenediamine (en) complexes of copper in the presence of H_2O_2. Figure 2 shows the kinetic curves of accumulation of O_2 as H_2O_2 was added to an aqueous solution of $Cu(en)_2^{2+}$ and the dependences of the changes in the concentrations (I/I_0) of the $Cu(en)_2(H_2O)_2^{2+}$ and $Cu(en)(H_2O)_4^{2+}$ complexes. Here, I_0 and I are the intensities of the high-field lines of the ESR spectra of the $Cu(en)_2^{2+}$ and $Cu(en)^{2+}$ complexes measured at the initial and at certain instants (or the value of the optical density D_{540} at λ = 540 nm). The data of ESR spectroscopy and spectrophotometry (see Figs. 2 and 3) confirm the stepwise character of transformations of $Cu(en)_2^{2+}$:

$$Cu(en)_2(H_2O)_2^{2+} \xrightarrow{k_1} Cu(en)(H_2O)_4^{2+} \xrightarrow{k_2} Cu(H_2O)_6^{2+}. \quad (4)$$

It can be seen from Fig. 3 that only the initial $Cu(en)_2(H_2O)_2^{2+}$ complexes occurred in the solution after 12 min. After 35 min, only $Cu(en)(H_2O)_4^{2+}$ complexes were present in the solution (within the experimental error), and $Cu(en)_2^{2+}$ complexes were absent. After 60 min, the number of the $Cu(en)^{2+}$ complexes decreased substantially as the concentration of the copper aqua $Cu(H_2O)_6^{2+}$ complexes increased. After 3 h, copper(II) ions occurred in the solution predominantly in the form of these aqua complexes. Note that no other complexes, for example, complexes that contain three or one N atom in the coordination sphere ($Cu(en)(NH_3)^{2+}$ or $Cu(en)(NH_2CHO)^{2+}$), were detected both at 298 K and at 77 K, *i.e.*, if such adducts were present in the solution, their concentrations should be less than $2 \cdot 10^{-4}$ mol L^{-1}. From Figs. 2 and 3 it also follows that the $Cu(en)(H_2O)_4^{2+}$ complex oxidizes substantially more slowly than the initial copper complex.

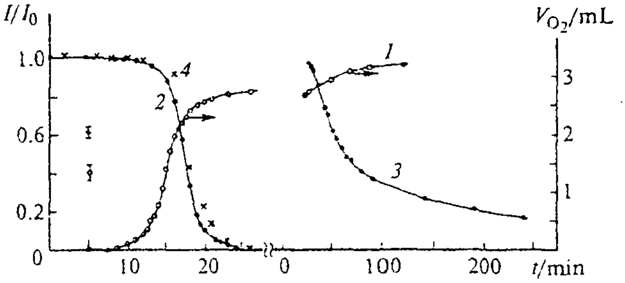


Fig. 2. Kinetic curves of elimination of O_2 (*1*) and the change in the concentration of $Cu(en)_2^{2+}$ (*2*) and $Cu(en)^{2+}$ (*3*) complexes based on the data of ESR spectroscopy (*2*, *3*) and spectrophotometry (*4*) upon addition of H_2O_2 to an aqueous solution of $Cu(en)_2^{2+}$ at 300 K ($[H_2O_2]_0$ = 0.3 mol L^{-1}; and $[Cu(en)_2^{2+}]_0$ = 0.003 mol L^{-1}).

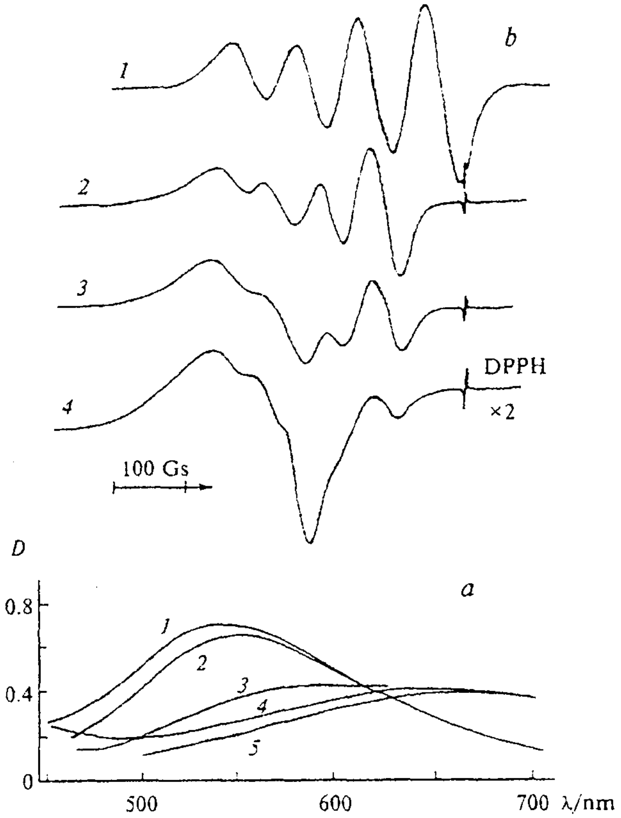


Fig. 3. Changes in the absorption spectra (*a*) and the ESR spectra (*b*) of aqueous solutions of copper complexes in the presence of H_2O_2 at 300 K ($[H_2O_2]_0$ = 0.3 mol L^{-1}; and $[Cu(en)_2^{2+}]_0$ = 0.003 mol L^{-1}). *a*, after 5 (*1*), 14 (*2*), 16 (*3*), 18 (*4*), and 35 min (*5*); *l* = 4 cm; *b*, after 12 (*1*), 35 (*2*), 60 (*3*), and 180 min (*4*).

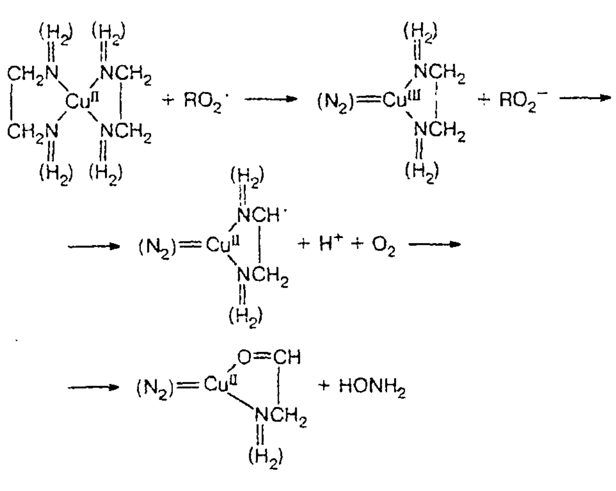
Oxidation of sulfur-containing RSH compounds. Complexes of transition metal ions with anion-exchange resins are active catalysts for oxidation of sulfur compounds by molecular oxygen.[1] The oxidation of RSH compounds proceeds according to reaction (2). In this case, a decrease in the number of N atoms coordinated to Cu in the polymer-metal complexes leads to a substantial decrease in the catalytic activity.[1,6] Unlike oxidation of hydrocarbons and decomposition of H_2O_2, in the case of oxidation of the RSH compounds, no changes are observed in the ESR spectra of the samples before the reaction and after completion of the reaction. Apparently, this is associated with the well-known fact that the reactivity of $RS^{\cdot}$ radicals is substantially lower that the reactivities of $R^{\cdot}$, $OH^{\cdot}$, and $RO_2^{\cdot}$ radicals. The stability of the copper complexes in the reactions of oxidation of sulfur compounds has been observed previously.[13,14]

A comparison of the parameters of the spin-Hamiltonians of the samples of the polymer-metal Cu(AN-521) complex and its low-molecular-weight analog, 1,2-diethylethylenediamine, which were used over a period of several hours in the reaction, provides evidence that only two secondary N atoms in the coordination sphere about Cu^{II} ions are present, whereas two other N atoms are replaced by oxygen-containing functional groups, apparently, by water molecules, which are present in the sample (see Table 1).

These changes are, apparently, associated with the oxidation of the polymeric matrix analogously to the scheme[15] for the catalytic decomposition of hydrogen peroxide with ethylenediamine complexes (Scheme 1).

Previously, the structural changes in the polymer-metal complexes were observed under the conditions of catalytic oxidation of *n*-dodecane by oxygen at 140 °C.[16] When Cu^{II} ions are sorbed by the AN-31 anion exchanger or its analog AN-31n, complexes of the $Cu(N)_4$ composition, which contain two $-NHCH_2CH_2NH-$ fragments of the chain of the cross-linked polyethylenepolyamine, form in the phase of the catalyst.[17] Figure 4 shows the dependences of the effective values of $g_{\parallel}$ and the hyperfine interaction constants $A_{\parallel}$ on the time of use of the catalysts. We constructed these dependences based on the published data.[16] During the first 2—3 h, the copper complexes remained unchanged, the reaction mixture contained predominantly hydroperoxides, and the amounts of other products were small.[16]

Scheme 1



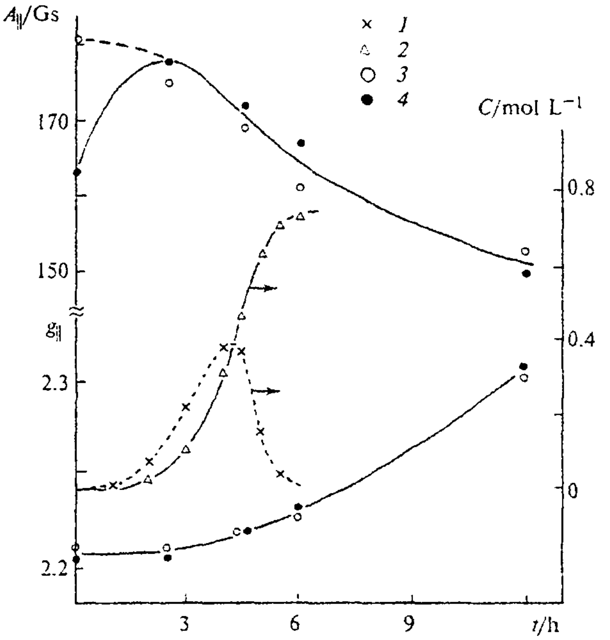


Fig. 4. Kinetic curves of accumulation of hydroperoxides ROOH (*1*) and the total amount (*2*) of final products (carboxylic acids + alcohols + carbonyl compounds) of oxidation of *n*-dodecane at 413 K and the change in the parameters $A_{\parallel}$ and $g_{\parallel}$ of the ESR spectra of the Cu(AN-31) (*3*) and Cu(AN-31n) (*4*) catalysts.[12]

When the catalysts were used for ~4 h, the polymer-metal complex underwent rapid rearrangement, which was associated with the protonation of the amino groups of the polymer and the decrease in the number of en-type five-membered rings in the tetraamine polymer-metal complex.[18] When the catalyst was used longer than 5 h, a new ESR signal (along with the spectrum of the polymer-metal $Cu(N)_4$ complex) appeared. Its amplitude increased rapidly, and after 6 h, the concentration of this complex in the sample was higher than 70%. The parameters of this new signal (see Table 1) are close to those observed in the amino acid solutions vitrified at 77 K[18] and correspond to the composition of the equatorial plane of the polyhedron of the polymer-metal Cu[1N,3O] complex, *i.e.*, to the complex with one N atom in the coordination sphere.

The appearance and the rapid increase in the number of complexes of this type occur simultaneously with the accumulation of the maximum amount and vigorous decomposition of hydroperoxides ROOH, the products of the first stage of catalytic oxidation of *n*-decane to the final products of the reaction, namely, to aliphatic alcohols, carbonyl compounds, and carboxylic acids.[16] Oxidation over a period of 6 h gave the products, which were ~60% carboxylic acids (see Fig. 4).

In the IR spectrum of the catalyst, which was used over a period of 6 h, a new band with maximum at 1720 cm^{-1}, which corresponds to the stretching vibration of the C=O bond of the protonated carboxyl groups,[19] appears.[16] This indicates that the oxidation of hydrocarbons is accompanied by the side oxidation of the matrix of the polyamine polymer-metal complexes with the formation of COOH groups, which take an active part in the formation of new Cu^{II} complexes with the modified AN-31 anion exchangers (see Fig. 4, Table 1).

Analogous changes in the composition and structures of the coordination spheres of the Cu^{II} complexes with commercial low-basic anion exchangers (AN-221×12P, AN-84×7P, AN-20×12P, and AN-21×12P) were observed in the studies of the oxidation of 2,3,6-trimethylphenol (TMP) by hydrogen peroxide.[20] Examination of the ESR spectra demonstrated (see Table 1) that the initial Cu(AN-221) and Cu(AN-84) complexes are of the $Cu(N)_4$ composition with the chelate five-membered rings of the ethylenediamine type. The Cu(AN-221) complex is analogous to Cu(AN-521), whereas the structure of the Cu(AN-84) complex is substantially tetrahedrally distorted due to the peculiarities of the structure of the matrix analogous to that of the AN-31 anion exchanger because both AN-84 and AN-31 were synthesized starting from polyethylenepolyamine. The samples of Cu(AN-20) and Cu(AN-21) contained $Cu(N)_2$ diamine complexes.

As a result of oxidation of 2,3,6-trimethylphenol by H_2O_2 in the presence of the anion-exchange catalysts, the initial polymer-metal complexes underwent substantial transformations. In the case of Cu(AN-20) and Cu(AN-21), the $Cu(N)_2$ complexes transformed into $Cu(N)_1$, and the remaining five vertices of the polyhedron are occupied by O atoms (see Table 1). The parameters of the ESR spectra of these polymer-metal complexes are very close to the values known for aminocarboxylic ampholites, which contain one aminocarboxylic group in the coordination center.[18] The polymer-metal complexes, which contain chelate rings, Cu(AN-221) and Cu(AN-84), are transformed into complexes with four N atoms belonging to different functional groups (the chelate effect is absent). In the case of Cu(AN-221), the $Cu(N)_2$ complexes are formed (see Table 1), along with the tetraamine complexes.[20] It was also observed that the subsequent use of these catalysts caused a gradual decrease in the catalytic activity owing to the rearrangement of the polymer-metal complexes, which, in our opinion, correlates with the decrease in the number of N atoms in the coordination sphere about the Cu atoms.[1,6,7]

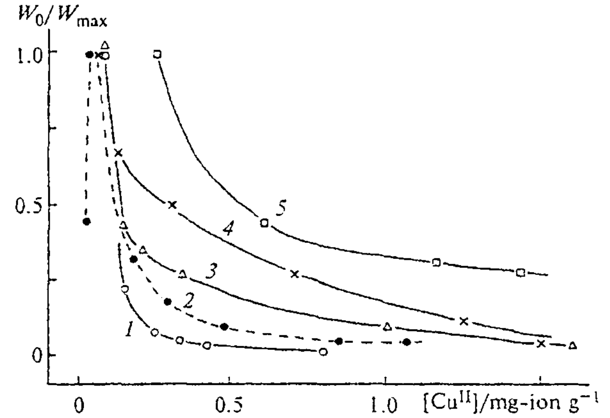


Fig. 5. Dependence of the relative catalytic activity on the concentration of Cu^{II} in the AN-521 (*1*), AN-221 (*2*), AN-31 (*3*), and EDE-10p (*4*, *5*) anion exchangers in the oxidation of cumene (*1*), C_4H_9SH (*2*, *3*), and Na_2S (*5*) by O_2 and decomposition of H_2O_2 (*4*).

In the case of the anion-exchange polymer-metal complexes, the factors that affect the processes of free diffusion of the reagents and the reaction products in the volume of catalyst granules should play a great role. Among these factors are the number of cross-linking agents, the degree of filling of the polymeric matrix with metal ions, and the nonuniformity of their distribution in granules. This effect either may be purely steric (a chemically inert cross-linking agent)[1,4] or may lead to a change in the structure of the catalytic centers of the polymer-metal complexes and in their distribution in the anion exchanger phase.

In our opinion, the change in the specific catalytic activity (per metal ion) as the concentration of Cu^{II} ions in the polymer-metal complex increases is analogous in character for a great variety of reactions and catalysts (Fig. 5). From the concentration $[Cu^{II}] > 0.05$ mg-ion g^{-1} and on, the specific catalytic activity decreases substantially. When only one type of the polymer-metal complexes occurs in the anion exchangers (AN-521, AN-511, and EDE-10p) throughout the $[Cu^{II}]$ concentration range, the decrease in the values of W_0/W_{max} (see Fig. 5) is attributable only to the fact that the diffusion in granules of the polymer-metal complex slows down.

The effect of the diffusion factors on the rapid decrease in the specific catalytic activity as the concentration of copper complexes in the anion-exchanger matrix increases is clearly shown in Fig. 6. In the studied range of copper concentrations in the AN-31 anion exchanger, only polymer-metal complexes of the type $[Cu(N)_4]$ are formed within the experimental error. The dependences in Fig. 6 are different in character, which indicates that most Cu^{II} ions in the AN-31 helium anion exchanger at $[Cu^{II}] > 0.4$ mg-ion g^{-1} are not involved in the oxidation of RSH, apparently due to

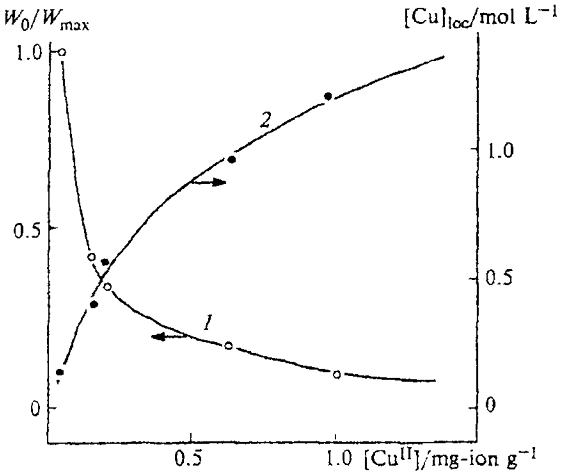


Fig. 6. Dependence of the average local concentration $[Cu]_{loc}$ of Cu^{II} complexes in AN-31 anion exchanger (*2*) and the relative catalytic activity W_0/W_{max} (*1*) in the oxidation of C_4H_9SH on the concentration of Cu^{II} in the sample.

the fact that free diffusion of RSH molecules into anion exchanger granules is sterically hindered (or due to the fact that the reaction products escape from the granules).

The concentration dependence of the initial rate of the reaction W_0 in the case of oxidation of 1-butanethiol by O_2 in the presence of Cu(AN-221) complexes can be explained analogously.[13] In the case of polyamine anion exchangers of this type, it was found[8,14] that "associates" of the polymer-metal complexes are formed in granules with a very high local concentration of copper ions even at $[Cu^{II}] \geq 0.05$—0.1 mg-ion g^{-1}. Apparently, diffusion of C_4H_9SH molecules into these associates with average distance between the copper ions $\langle r \rangle \approx 0.7$—0.8 nm[21] is substantially hindered.

The reported results demonstrated that in the course of the catalytic redox reactions, polyamine polymer-metal complexes undergo substantial transformations. If in the case of liquid-phase oxidation of organic compounds by O_2, H_2O_2, or organic hydroperoxides, a readily oxidized group is in the immediate vicinity of the coordinating atom of the ligand or this atom belongs to the oxidized group, the oxidation of these functional groups occurs as a side reaction. As a result, the composition and structure of the coordination centers are changed, namely, the number of coordinated N atoms decreases, and the number of O atoms in the polymer-metal complexes increases. In this case, the polymeric matrix undergoes chemical modifications.

This work was supported by the Russian Foundation for Basic Research (Project No. 95-03-09715).

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Received November 26, 1996;
in revised form February 12, 1997