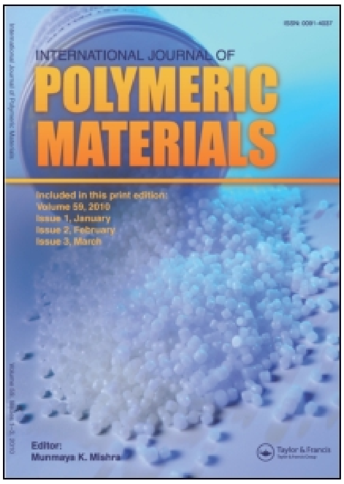

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Oxidative Processes in Polymer-Metal Complexes: A New Way to Prepare Polyampholytes with Groups of α-Picolinic Acid

A. I. Kokorin[a]
[a] N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

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Oxidative Processes in Polymer–Metal Complexes: A New Way to Prepare Polyampholytes with Groups of α-Picolinic Acid

A. I. KOKORIN

N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
Kosygin St. 4, Moscow, 117977, Russia

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The catalytic reaction of hydrogen peroxide decomposition in aqueous solution in the presence of Cu(II)-containing ion-exchange resins of the poly-α-picolinic type (AN-25, AN-251) was studied. It has been shown using the EPR and IR spectroscopies that in these polymers the methyl groups of the 2-methyl-5-vinylpyridine residues are oxidized to carboxyl groups forming fragments of α-picolinic acid, producing a new chelating ion-exchanger.

Keywords: Anion exchange resins; degree of crosslinking; Cu(II) complexes; H_2O_2 decomposition

AIMS AND BACKGROUND

Polyampholytes containing complexing groups of α-picolinic acid are very well known both as water soluble macromolecules and selective ion-exchange resins [1, 2], wide-spread as absorbents of heavy metal cations in hydrometallurgy and for water purification [3, 4]. Metal complexes of such polymers were used as catalysts for different redox reactions [5, 6].

The traditional method to synthesize polymers with 2-carboxypyridine residues (ANKB-2) is based on the reaction of the macroporous anionite AN-251 (see below) with formaldehyde and further oxidation of the product by nitric acid [2, 7]. This method allows to receive commerical polyampholytes of rather good quality, but its essential deficiency is connected with high toxicity of the process and with a possible danger for the environment polution.

A new approach to solve this problem has been recently made [8]. It was suggested to oxidize the initial co-polymer of 2-methyl-5-vinylpyridine with *p*-divinylbenzene by aqueous solutions of hydrogen peroxide H_2O_2 after preliminary treatment of the co-polymer with methanol solutions of $Cu(NO_3)_2$ or $FeSO_4$. The procedure performed very good results (Tab. I) but, however, nothing has been defined about the mechanism of chemical reactions passed in the polymer–metal system.

The main goal of the present work is to report our results on an investigation of the composition and structural changes taking place during the reaction of H_2O_2 decomposition in the presence of Cu(II) complexes with anion-exchange resins of the vinylpyridine series.

EXPERIMENTAL

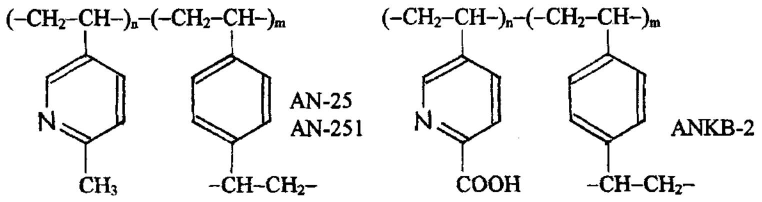
The anion-exchange gel resin AN-25, its macroporous analog AN-251 and the commercial ampholyte ANKB-2 have the following structures:

The degree of cross-linking in the resins was equal to 8%. The procedure used in treating the resins to remove inorganic materials and low molecular weight impurities is set forth in [9], as is the procedure for obtaining nonprotonated and partially protonated

TABLE I Conditions of the reaction and characteristics of the ampholytes obtained*

Metal ion	*Metal content in the resin, mg-ion/g*	*H_2O_2 concentration, mol/l*	*Absorption capacity, mg-ion/g*	
			By 0.1 *N HNO_3*	*By* 0.1 *N NaOH*
Cu(II)	3.3	0.55	1.0	2.5
Cu(II)	2.2	0.2	1.3	2.4
Cu(II)	1.35	0.55	2.1	2.0
Cu(II)	2.2	0.02	2.3	1.8
Fe(II)	0.22	0.55	0.4	3,7
Fe(II)	0.08	0.2	1.1	3.0
Fe(II)	0.02	0.02	1.5	2.7

* The initial ionite AN-251 had the absorption capacity only by HNO_3 equal to 4.5 mg-ion/g.



SCHEME 1

forms of the anion-exchange resins. The pH was measured in a "pH-262" potentiometer.

Complexes of Cu(II) with AN-25, AN-251 and ANKB-2 were obtained by treating the resins with aqueous solutions of copper nitrate (analytically pure grade) with various concentrations, for 48 hours at 20°C under static conditions. After equilibrium has been established, the concentration of uncomplexed copper was determined by compleximetric titration.

The kinetics of H_2O_2 decomposition were investigated by measuring O_2 evolution, using a volumetric method (accuracy of measurement ±0.1 ml). The kinetic curves (will be published elsewhere), without any induction period, were used to calculate the initial rate W_0 of H_2O_2 decomposition. At the end of the experiment, the solution was analyzed to determine the concentrations of undecomposed H_2O_2 and Cu(II) ions. It was established that the AN-25 and AN-251 have practically no catalytic activity in the absence of Cu(II).

The EPR spectra were recorded using a "Varian E-4" X-band radiospectrometer in quartz tubes 4 mm in diameter at 77 K. Magnetic field was graduated by the spectra of Mn^{2+} in the MgO matrix and by the DPPH ($g_0 = 2.0036$). For determining the composition of the coordination sphere of copper complexes with AN-25 and AN-251, we used data from [10] on the complexation of Cu(II) with 2-methyl-5-ethylpyridine (2M5EP). The IR spectra of the substances (in the KBr tablets) were recorded using a "Specord-75 IR" spectrometer.

RESULTS AND DISCUSSION

From the analysis of kinetic curves for the evolution of O_2 during the process of H_2O_2 decomposition and the values of the calculated W_0

(Tab. II) one can see that for the anion-exchange resins, containing α-picolinic groups, increases in the degree of protonation α of the pyridine units of the polymer lead to significant decreases in the rate of O_2 accumulation. The observed decrease in W_0 by more than an order of magnitude when the resin granules receive a presorption treatment with aqueous HNO_3 solution (with a change in α from 0 to 0.8 or higher) can be explained by changes in the composition and structure of the coordination sphere of the complexes.

Measurements of the principal values of the g-factor and the hyperfine constant (HFC) $A_{\|}$ (Tab. II) showed that, beginning with $\alpha \geq 0.4$, the values of $A_{\|}$ decrease monotonically, whereas the values of $g_{\|}$ increase. This sort of changes in parameters of the spin-Hamiltonian are related to the decrease in number of nitrogen atoms in the complex of Cu(II) upon protonation of some of the pyridine groups of the macromolecular ligand, analogous to what was observed in [9, 11]. I should be noted that the values listed in Table II for $g_{\|}$ and $A_{\|}$ with $\alpha \geq 0.4$ are effective values (they do not characterize an individual type of the complex). The reason for this is a broad linewidth in the EPR spectra of copper with AN-25, such that it is impossible to determine the fraction of complexes of each type with any satisfactory degree of accuracy. By comparing the measured parameters with the data of [10], however, we can draw the conclusion that, in the case of the AN-25 resin and the similar macroporous resin AN-251, at $\alpha < 0.4$, the major part of the complexes can be assigned to the type $Cu(PY)_3^{2+}$, and when $\alpha \rightarrow 1$, to the $Cu(Py)_2^{2+}$ type.

It is difficult to find any rigorous quantitative correlation between the kinetic and structural data (Tab. II), since the two sets of data were

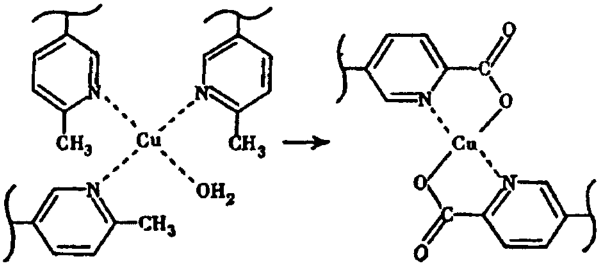
TABLE II Initial rate of H_2O_2 decomposition of W_0 at 313 K and parameters of EPR spectra of Cu(II) complexes with a resin AN-25 at 77 K in relation to degree of protonation α. [Cu(II)] = 0.005 mg-ion/g

	$W_0 \cdot 10^4$,	*Before reaction*		*After reaction*	
α	*moles/l·s·mg-ion*	$A_{\|} \pm 3$, *G*	$g_{\|} \pm 0.005$	$A_{\|} \pm 3$, *G*	$g_{\|} \pm 0.005$
0	12 ± 1	161	2.280	170	2.258
0.2	9.0 ± 1	162	2.281	170.5	2.253
0.4	6.7 ± 0.8	160	2.283	172	2.255
0.6	3.1 ± 0.4	157	2.286	171.5	2.250
0.8	1.1 ± 0.1	155	2.291	172.5	2.254
$\rightarrow 1$	0.25 ± 0.05	149	2315	172	2.254

obtained at considerably different temperatures (313 and 77 K). From the data of Table II it follows that a decrease in the coordination number with respect to nitrogen in the complexes Cu(AN-25) leads to a considerable lowering of the catalytic activity of these complexes. A decrease in the number of pyridine groups in the complex from 3 to 2 leads to a several-fold reduction of W_0, by a factor of 5 – 10. A similar ratio of the initial rates was obtained in [9] for the reaction of the liquid-phase oxidation of *n*-butyl mercaptan by O_2 in the presence of Cu(AN-251) complexes.

A conclusion that, when the number of nitrogen-complexing pyridine groups of the resin in the coordination sphere of the Cu(II) ion is increased, this is accompanied by a considerable increase in the catalytic activity in H_2O_2 decomposition, and is in agreement with results reported in [9, 12] for other redox reactions.

In studies of the process of liquid-phase oxidation of organic compounds by O_2 [13, 14], it was established that partial oxidation of the polymer matrix of the resin was observed as a result of occurrence of a catalytic reaction. This leads to a rearrangement of the coordination sphere of the polymer–metal complex. According to this idea one can see from Table II that, in the case of the AN-25, the values of $A_{||}$ increase and the values of $g_{||}$ decrease as a result of the reaction, down to values corresponding to the complex of Cu(II) with the ampholyte ANKB-2 ($A_{||} = 172$ G, $g_{||} = 2.250$) [15], which contains complexing groups of α-picolinic acid. For the Cu(AN-251) with $\alpha = 0$, changes were observed in the parameters: $A_{||}$ from 158.5 to 171.5 Oe, and $g_{||}$ from 2.290 to 2.249. Thus, in the decomposition of H_2O_2 on Cu(AN-25) or Cu(AN-251), the methyl group of the pyridine ring is oxidized to carboxyl:



SCHEME 2

The structural and chemical changes in the heterogeneous complexes of copper with AN-251 ion-exchange resin during the process of H_2O_2 decomposition could be explained by the reactions of activation of both H_2O_2 and O_2 on the catalyst; then the process develops further by both a molecular and a radical mechanism, for instance [16]:

$$[Cu^{2+}] + H_2O_2 \rightarrow [Cu^{+}] + HO_2^{\cdot} + H^{+}$$

$$[Cu^{+}] + O_2 \leftrightarrow [Cu^{2+} \ldots HO_2^{-}]$$

$$[Cu^{2+} \ldots HO_2^{-}] + RH \rightarrow \begin{cases} [Cu^{2+}] + HO_2^{-} + R^{\cdot} \\ [Cu^{+}] + ROOH, \end{cases}$$

where R is the 2-methylpyridine fragment.

The process $R{-}CH_3 \rightarrow R{-}COOH$ is also proved by the substantial changes in the IR spectra of the catalyst, particularly the significant decreases in intensity of the absorption bands at 1370 and $1420\,cm^{-1}$, which correspond to bending vibrations of CH_3 groups in the picolinic fragment (Fig. 1). The greatest change in the IR spectra is the appearance of intense bands in the $1640-1730\,cm^{-1}$ region, corresponding to vibrations of carboxyl groups in picolinic acid fragments (both free and bound to copper ions (*cf.* [17, 18]). The oxidation of the CH_3 groups is apparently accomplished within the complex, since we were unable to detect any yield of free-radical intermediates by means of spin traps such as Ionol or *N*-tert-butyl-α-phenylnitrone in the solution.

Figure 2 shows changes in $g_{\|}$ and $A_{\|}$ magnitudes measured at different times of the reaction for two concentrations of Cu(II) ions. It is seen that reconstruction of the coordination sphere in AN-251 passes much faster at lower amount of copper ions in the polymer matrix.

Protonation of the anion-exchange resins in the process of presorptive treatment ($\alpha \rightarrow 1$) does not affect the structure of coordination sphere of the complexes after the reaction (Tab. II). For the AN-25 and AN-251, this can be explained quite easily, since the stability constants of the chelate complexes that are formed, Cu[2N, 2O], the same as for ANKB-2, are extremely high and are practically independant on protonation of the original resin.

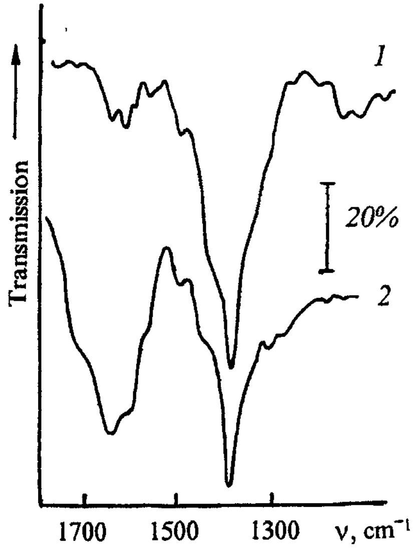


FIGURE 1 IR spectra of complexes Cu(AN-251): 1 – original catalyst; 2 – after 1 hour of acting in the process of H_2O_2 decomposition at 298 K. $[H_2O_2] = 0.2\,M$; $m_{cat} = 0.6\,g/l$.

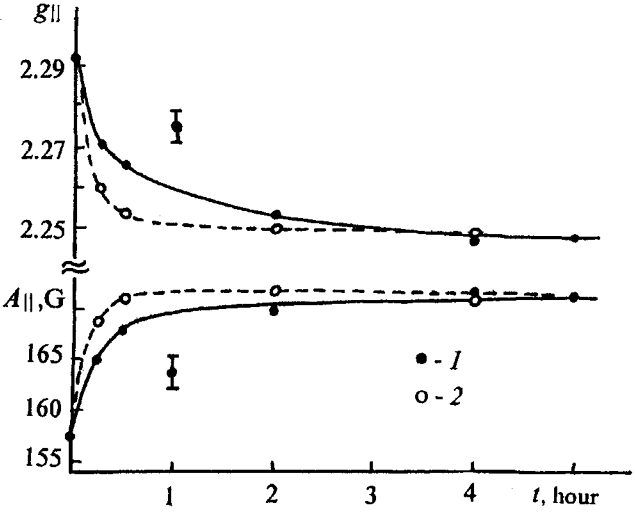


FIGURE 2 Changes of the EPR parameters $g_{\|}$ and $A_{\|}$ for the complexes Cu(AN-251) contained 0.5 (1) and 0.084 mg-ion/g (2) copper ions on the acting time in the process of H_2O_2 decomposition at 293 K. $[H_2O_2] = 0.1\,M$.

CONCLUSION

All the data obtained by EPR and IR spectroscopy allows to conclude that the matrix of Cu(II)-containing ion-exchange resins of the poly-α-picolinic type undergoes deep-seated changes in the course of the catalytic decomposition of H_2O_2, in particular, the methyl groups of the 2-methyl-5-vinylpyridine branches are oxidized to form fragments of α-picolinic acid, producing a new chelating ion-exchanger.

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