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Reactivity of the Peroxo Complexes of Copper(II) Hydroxide

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Abstract—In the interaction with H_2O_2 in an alkaline medium, $Cu(OH)_2$ forms terminal Cu–OOH and bridging peroxo complexes with the μ-1,1 and μ-η^2:η^2 structures. It was found that the terminal peroxide is active in the reactions of H_2O_2 decomposition, diphenol oxidation, and nitrile conversion into acid amides. The promoting effect of ammonia on these reactions was found. A possible mechanism is discussed.

INTRODUCTION

The main function of many copper-containing enzymes consists in the binding, activation, or reduction of oxygen. Their action can be modeled in two ways: by the development of functional or structural analogs. Published data indicate that the mechanisms of enzyme operation have been studied mainly by the latter way. For this purpose, a great number of structurally different peroxo complexes of copper with various polydentate organic ligands were synthesized [1–3]. The majority of these complexes exist at low temperatures; they are water insoluble and often unsuitable for studying the reactivity toward external substrates because, as a rule, their active oxygen is consumed in the oxidation of their own ligands.

Previously [4], we found that colloidal copper hydroxide and copper hydroxide supported on silica gel form a number of peroxo complexes by interaction with H_2O_2 in aqueous solutions at pH 8–11. The electronic spectra of these complexes are very similar to the published spectra of complexes with organic ligands. Moreover, the catalytic oxidation of light hydrocarbons [5], pyrocatechol, and benzene [6] was found to occur in these systems. Because it was found that the catalytic decomposition of H_2O_2 and the oxidation of substrates occur by a nonradical mechanism, the assumption was made that this is due to the participation of peroxides in a catalytic cycle.

This work is the continuation of a study of the catalytic properties of $Cu(OH)_2$ and the structures and properties of peroxo complexes and reaction intermediates by spectroscopic techniques.

EXPERIMENTAL

Chemically pure $Cu(NO_3)_2$, NaOH, $Ba(NO_3)_2$, and NH_4NO_3 and starch for iodometry were used in this study. Acetonitrile (high-purity grade), benzonitrile (chemically pure), and resorcinol (chemically pure) were used without additional purification.

Electronic spectra were measured on UVICON 923 and Specord M-40 spectrophotometers; EPR and IR spectra were measured on Bruker ER-200D and FTIR Bomem MB-102 spectrometers, respectively. The particle size distribution was studied by small-angle X-ray scattering (SAXS) in a KRM-1 chamber using CoK_α radiation.

Deionized water was used for preparing solutions.

The reaction kinetics was studied in a reactor thermostated at 298 K; two samples were taken at certain time intervals: one of them was used for recording absorption spectra and the other was used for measuring the concentration of H_2O_2 by the reaction with Ti(IV).

Preparation of a colloid $Cu(OH)_2$ solution stabilized with starch. Starch (250 mg) was dissolved in 50 ml of hot water. After cooling, 0.2 ml of a 0.27 M $Cu(NO_3)_2$ solution was added to the above solution; then, 1.25 ml of 2 M NaOH was added with very intense stirring. The resulting solution contained 1×10^{-3} M $Cu(OH)_2$, 0.05 M NaOH, and 0.5 wt % starch. To prepare solutions with other hydroxide, alkali, and starch contents, the volumes of the initial reagents and the weighed portions of starch were proportionally changed.

Isolation of a benzonitrile reaction intermediate. Ethanol (30 ml), benzonitrile (0.9 ml), and water (55 ml) were mixed. The resulting solution was placed in an ice bath; next, 1.6 ml of a 2.8 M H_2O_2 solution, 0.5 ml of a 0.27 M $Cu(NO_3)_2$ solution, and 1.8 ml of a 1 M NaOH solution were added to it. After stirring for 10 min, a pink precipitate was filtered off and washed with ethanol and diethyl ether. The yield was 35 mg.

RESULTS

Catalytic decomposition of hydrogen peroxide. On the addition of H_2O_2 to colloidal $Cu(OH)_2$, its color was changed from blue to yellow. Figure 1 demonstrates the absorption spectrum of colloidal $Cu(OH)_2$ (curve *1*) in a 0.01 M NaOH solution. The spectrum exhibits a

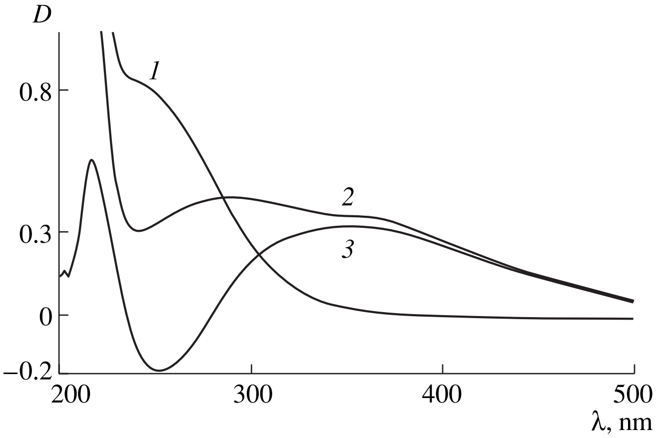


Fig. 1. Absorption spectra of a 1×10^{-3} M $Cu(OH)_2$ colloid solution stabilized with 0.5 wt % starch in a 0.01 M NaOH solution (*1*) in the absence and (*2, 3*) in the presence of 0.025 M H_2O_2. Reference solutions: (*1, 2*) 0.5 wt % starch and 0.01 M NaOH; (*3*) a colloid without H_2O_2. The cell thickness is l = 0.2 cm.

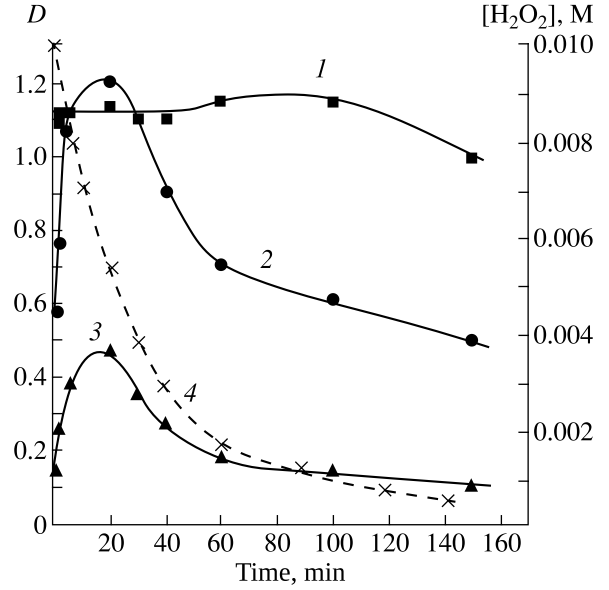


Fig. 2. Absorption band intensities at (*1*) 280, (*2*) 360, and (*3*) 440 nm and (*4*) the concentration of H_2O_2 as functions of time. 0.9×10^{-3} M $Cu(OH)_2$; 0.5 wt % starch; 0.01 M H_2O_2; pH 10; l = 1 cm.

weakly pronounced maximum at ~240 nm. The intensity of this absorption increased as the alkali concentration was increased up to 0.05 M (Fig. 3, spectrum *1*) and remained unchanged as the alkalinity of the solution was further increased. Such a behavior is characteristic of complexation equilibria; therefore, this band can be ascribed to the $OH^- \longrightarrow Cu$ charge-transfer band. On the addition of H_2O_2, the band intensity at 240 nm significantly decreased and new diffuse bands appeared at 280–290 and 350–360 nm (Fig. 1, spectrum *2*). It is evident that under these conditions the major portion of copper is bound in peroxo complexes. The absence of a signal from the EPR spectra of this solution indicates that individual copper ions are not formed under the action of H_2O_2: peroxides are either the constituents of a $Cu(OH)_2$ polymer or exhibit a binuclear structure. In the majority of experiments, changes in the spectra of colloidal $Cu(OH)_2$ in the presence of H_2O_2 were weakly pronounced. Therefore, we mainly measured the spectra with the use of the parent colloid as a reference solution before the addition of H_2O_2. The presence and concentration of a peroxide that absorbs at 280 nm can be judged from the depth of a minimum at 250–270 nm in the negative portion of this difference spectrum (Fig. 1, spectrum *3*).

As H_2O_2 was consumed, the peroxide absorption band intensities decreased, whereas the intrinsic absorption bands of $Cu(OH)_2$ at 240 nm increased. In this case, an isosbestic point, which was observed at 270 nm, indicates that $Cu(OH)_2$ turned back into its initial state directly from a complex that absorbs at 280 nm.

The Gaussian deconvolution of the absorption spectra of colloidal $Cu(OH)_2$ in the presence of H_2O_2 revealed, in addition to the absorption bands at 280 and 360 nm, another peroxo complex that absorbs at 440 nm. All three peroxides were different from each other in the kinetics of formation and decomposition (Fig. 2). Thus, the absorption band at 280 nm appeared immediately after the addition of H_2O_2, and its relative intensity changed only slightly with time. At the same time, the absorption band intensities at 360 and 440 nm initially increased and then decreased at different rates: $t_{1/2}$ = 36 and 20 min, respectively. Because of this, the $A_{360} : A_{440}$ absorbance ratio increased from 2 at the beginning of the reaction to 4–5 at the end. Moreover, at the initial time of reaction, this ratio strongly depended on conditions: it increased as the concentration of NaOH was increased or as the concentrations of H_2O_2 and the catalyst were decreased (Table 1). This implies that high alkali concentrations are more favorable for the formation of a peroxide that absorbs at 360 nm, whereas the relative fraction of the second complex increases at low NaOH, H_2O_2, and copper contents. Thus, optimum conditions for the formation of peroxides that absorb at 360 and 440 nm differ considerably; this fact confirms that the peroxides are different in nature.

As the concentration of NaOH was increased from 0.01 to 0.1 M, the intensities of absorption bands due to peroxides considerably decreased. This fact is indicative of competition between the hydroxyl ion and H_2O_2 for coordination sites at the copper ion (Table 1). A change in the starch content from 0.25 to 2% had the same effect, which can be explained in the same manner. Previously [7], we noted that chemical bonds are formed between starch and hydroxides because of the interaction of their hydroxyl groups; this fact explains the very good ability of starch to stabilize hydroxide colloids.

Effect of ammonia. Previously [4], we found that the rates of decomposition of both H_2O_2 and peroxo complexes considerably increased on the addition of bipyridyl or phenanthroline, which form stable complexes with copper and can break hydroxyl bridges in a polymeric $Cu(OH)_2$ molecule, to the test solutions. At the same time, pyridine had no pronounced effect on the reaction kinetics. In this study, we extended this range of ligands and used ammonia, a favorable difference of which from the above compounds consists in the absence of intrinsic absorption at $\lambda > 230$ nm. This allowed us to observe the behavior of the test colloids by measuring their spectra in the UV region.

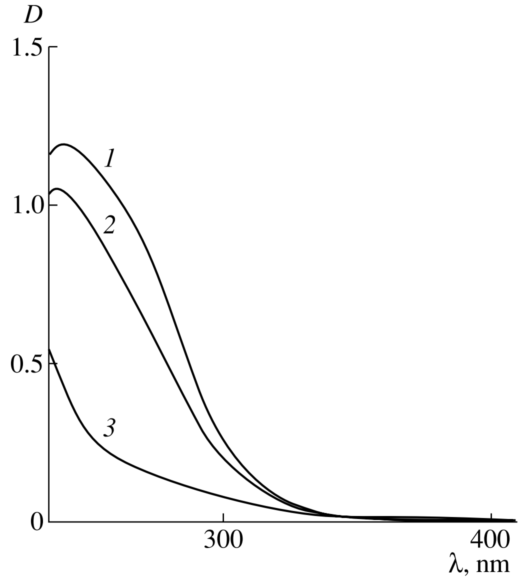


Fig. 3. Absorption spectra of a 1×10^{-3} M $Cu(OH)_2$ colloid solution stabilized with 0.5 wt % starch (*1*) in the absence and (*2, 3*) in the presence of 0.03 M NH_3. [NaOH] = (*1, 2*) 0.05 or (*3*) 0.01 M; $l = 0.2$ cm.

Figure 3 demonstrates the absorption spectra of colloidal $Cu(OH)_2$ in the absence and presence of NH_3. Changes were observed over the entire spectral range; however, the strongest changes were detected in the UV region. In particular, the relative intensity of the $OH^- \longrightarrow Cu$ charge-transfer band at 240 nm decreased; the most considerable decrease was observed in a 0.01 M alkali solution (where competition between OH^- and NH_3 is insignificant), as compared with a 0.05 M solution (Fig. 3). Spectral changes in the presence of NH_3 suggest the partial replacement of the OH^- groups of the hydroxide by ammonia with the formation of a mixed ammonia–hydroxyl environment at copper ions. This can be accompanied by the rupture of hydroxyl bridges and by a decrease in the size of colloid particles, as supported by SAXS. The first stability constants of copper complexes with OH^- and ammonia are 3.4×10^7 and 7.1×10^5 l/mol, respectively; that is, under appropriate conditions these ligands can compete with each other. However, complete conversion into ammonia complexes does not take place because, in the absence of starch, $Cu(OH)_2$ precipitates are formed in the test reaction mixtures either with NH_3 additives or without them.

Table 1. Absorbance of the peroxo complexes of copper hydroxide at the initial time and the initial rates of H_2O_2 decomposition (w_0) under different conditions

$[Cu] \times 10^3$, M	Starch, wt %	[NaOH], M	$[H_2O_2]$, M	$w_0 \times 10^3$, mol l^{-1} min^{-1}	D^{*}_{250}	D^{**}_{360}	D^{**}_{440}	D_{360}/D_{440}
1	0.5	0.01	0.025	2.0	−0.81	1.64	0.81	2.05
		0.05		3.2	−0.30	0.29	0.13	2.23
		0.1		0.8	−0.22	0.12	0.039	3.03
		0.05	0.05	4.9	−0.76	1.24	0.64	1.94
		0.1		2.5	−0.34	0.26	0.10	2.6
	1.0	0.01	0.025	1.6	−0.61	1.52	0.76	2.0
		0.05		1.9	–	0.27	0.11	2.45
		0.1		0.6	−0.2	0.12	0.035	3.38
		0.05	0.05	4.0	–	0.93	0.46	2.0
2	0.5	0.05	0.025	4.5	−0.49	0.61	0.32	1.95
		0.1		2.2	−0.17	0.17	0.072	2.31
		0.05	0.05	8.7	−0.87	1.53	0.82	1.87
		0.1		6.5	−0.34	0.40	0.19	2.1

* *D* found from difference spectra (reference solution: colloid); the cell thickness was 0.2 cm.

** The cell thickness was 1 or 0.5 cm for colloid concentrations of 1×10^{-3} and 2×10^{-3} M, respectively.

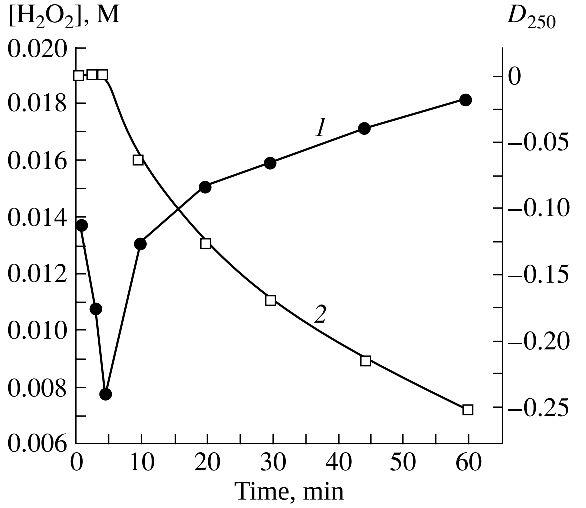


Fig. 4. (*1*) Absorbance at 250 nm and (*2*) the concentration of H_2O_2 in the presence of ammonia as functions of time. 1×10^{-3} M $Cu(OH)_2$; 2 wt % starch; 0.019 M H_2O_2; 5×10^{-3} M NH_3; 0.1 M NaOH; reference solution, a reaction mixture of the same composition without H_2O_2; $l = 0.2$ cm.

Low ammonia concentrations practically did not affect both the absorbance of solutions and the rate of H_2O_2 decomposition (Table 2). However, the kinetic curves of H_2O_2 consumption exhibited an induction period (Fig. 4, curve *2*), during which the concentration of a peroxide that absorbs at 280 nm increased. This manifested itself as the deepening of the minimum in difference spectra; that is, the absolute values of A_{250} increased (Fig. 4, curve *1*). The concentrations of all peroxides and the rate of H_2O_2 decomposition increased with ammonia concentration (Table 2); in this case, the induction period was absent. As distinct from the ammonia-free reaction mixtures, a band at 280 nm disappeared simultaneously with the consumption of H_2O_2 (cf. curves *1* in Figs. 2 and 4). As a consequence of the rapid simultaneous consumption of both a peroxo complex and H_2O_2 in the presence of 0.03 M NH_3, the reaction rates were higher than that at a 0.02 M concentration, whereas the values of A_{250} measured at the initial time were lower in magnitude (Table 2).

In the absence of ammonia, the rate of H_2O_2 decomposition passed through a maximum in the NaOH concentration order 0.01, 0.05, and 0.1 M (Table 1). With NH_3 added even in minimum amounts, the reaction rate in a 0.01 M alkali solution was much higher than that at higher NaOH concentrations; this reaction rate was very high so that it could not be measured by the technique used under these conditions.

Conversion of nitriles into acid amides. Colloidal $Cu(OH)_2$ catalyzes the oxidation of light hydrocarbons (ethylene, ethane, and methane) [5]. Because the water solubility of these gases is low, we attempted to use aqueous organic mixtures to increase it. In this case, we found that a copper colloid exhibited interesting properties in aqueous acetonitrile solutions. Acetonitrile additives to the reaction mixtures had no pronounced effect on the spectrum of the colloid; however, in the presence of H_2O_2 a new absorption band appeared at 540 nm. In this case, the color of the solution became pink, and the EPR spectra exhibited a signal, which corresponds to isolated copper ions with an N-containing

Table 2. Absorbance of the peroxo complexes of copper hydroxide at the initial time and the initial rates of H_2O_2 decomposition (w_0) in the absence and presence of NH_3

Starch, wt %	[NaOH], M	[NH_3], M	$w_0 \times 10^3$, mol l^{-1} min^{-1}	D^*_{250}	D^{**}_{360}	D^{**}_{440}
0.5	0.05	–	3.2	–0.30	0.29	0.13
		0.005	3.0	–0.29	0.25	0.11
		0.01	4.3	–0.48	0.72	0.34
		0.02	5.7	–0.51	0.75	0.34
		0.03	6.7	–0.44	0.8	0.34
	0.1	–	0.8	–0.22	0.12	0.039
		0.01	0.8	–0.24	0.10	0.039
		0.02	2.3	–0.33	0.16	0.06
		0.03	4.8	–0.43	0.23	0.085
1.0	0.1	-	0.6	–0.20	0.12	0.035
		0.01	0.7	–0.14	0.065	0.023
		0.02	2.1	–0.47	0.16	0.055
		0.03	3.3	–0.37	0.23	0.09

* *D* found from difference spectra (reference solution: colloid); the cell thickness was 0.2 cm.

** The cell thickness was 1 cm; [$Cu(OH)_2$] = 1×10^{-3} M; [H_2O_2] = 0.025 M.

ligand [8]. After the complete decomposition of H_2O_2, the band at 540 nm, as well as the EPR signal, disappeared, the spectrum of the colloid returned to the initial state, and acetamide was detected in the reaction mixture by gas chromatography.

The formation of a pink complex was not observed in colloid solutions with a high copper concentration and a low starch content, that is, under conditions when the fraction of coarse particles and peroxides that absorb at 360 and 440 nm in the colloid is high.

In the absence of starch, the reaction mixtures with acetonitrile additives always contained yellow precipitates of the peroxo complexes of copper hydroxide at the initial time after the addition of H_2O_2. These peroxo complexes gradually transformed into a pink complex and dissolved. In this case, the more hydrogen peroxide added, the slower the formation of a pink species.

Benzonitrile forms an analogous pink complex, which was isolated because of the low solubility of benzonitrile in water. The IR spectrum of this intermediate did not exhibit a relatively intense absorption band at 2233 cm^{-1}, which is characteristic of triple-bond C≡N vibrations; however, a new absorption band appeared at 3208 cm^{-1}, which was attributed to N–H-bond stretching vibrations [9]. Because only one absorption band was observed in this region, it is evident that only one hydrogen atom was attached to nitrogen. Thus, the intermediate contained the C=NH group. The presence of low-intensity but clearly defined bands at 3036 and 3041 cm^{-1} and intense absorption bands in the regions 1650–1500 and 710–690 cm^{-1}, which can be attributed to =C–H stretching vibrations, skeleton C=C in-plane vibrations, and C–H out-of-plane bending vibrations, respectively [9], indicates that the benzene ring was retained in the intermediate. Note that absorption bands characteristic of double-bond C=N vibrations were observed in the same spectral range as skeleton C=C in-plane vibrations in aromatic compounds. However, because several sufficiently intense absorption bands were observed in the region 1650–1500 cm^{-1}, it is obvious that a portion of them can be attributed to C=C-bond vibrations and a portion, to C=N-bond vibrations.

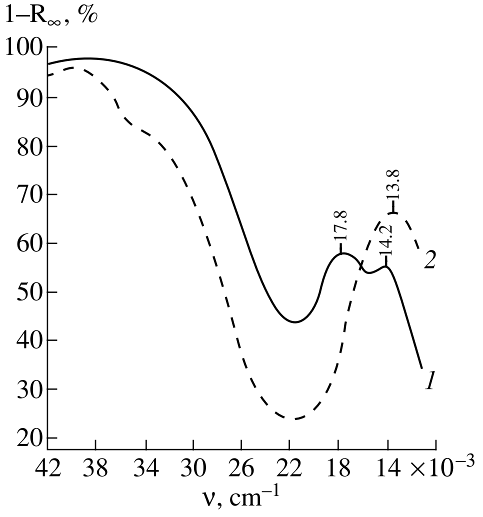
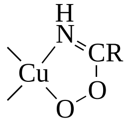


Fig. 5. Electronic diffuse-reflectance spectra of (*1*) an intermediate of the reaction of $Cu(OH)_2$ with H_2O_2 and benzonitrile and (*2*) $Cu(OH)_2$.

Figure 5 demonstrates the electronic diffusion-reflectance spectrum of the test reaction intermediate with benzonitrile. The spectrum exhibited absorption bands in the region 500–750 nm, which are typical of *d–d* transitions in the Cu^{2+} ion. A comparison of this spectrum with the spectrum of copper hydroxide, in which copper ions have a purely oxygen environment, suggests considerable differences between them. The electronic diffusion-reflectance spectrum of the test sample exhibited an absorption band at 556 nm in addition to an absorption band at 714 nm. This fact indicates that the nitrogen atom also enters the immediate environment of copper ions. An interesting peculiarity of this spectrum is a shift of charge-transfer bands to the low-frequency region; this is unusual because the occurrence of nitrogen atoms in the first coordination sphere should result in the opposite effect. The observed effect can be explained by the occurrence of a peroxo ligand in the first coordination sphere of copper ions; this was supported by the presence of absorption bands at 896, 871, and 842 cm^{-1}, which are characteristic of O–O-bond vibrations [10], in the IR spectrum. The results are consistent with published data [11, 12]; in these publications, a split absorption band due to the O–O bond was found for complexes of the L · CuOOR type with frequencies close to those observed in this work. As for the absorption bands that correspond to Cu–O- and Cu–N-bond vibrations, absorption bands at 592, 521, and 397 cm^{-1} can be assigned to them; this assignment is also consistent with published data [11, 12]. A more detailed analysis of electronic and IR spectra will be reported elsewhere.

These results together with EPR data allowed us to assume the following structure for the synthesized complex with peroxycarboximide acid:



Resorcinol oxidation. Previously [6], we found that copper and iron hydroxides catalyze the oxidation of pyrocatechol to α-hydro-β-hydroxymuconic acid γ-lactone; that is, this substrate undergoes oxidation with benzene ring opening and the transfer of two oxygen atoms. It was found that this product was also formed from resorcinol. In an alkaline medium, resorcinol exhibited an absorption band at 290 nm (ε = 3000 l $mol^{-1}cm^{-1}$). In a colloidal $Cu(OH)_2$ solution, the parameters of this band remained unchanged, as distinct from that of pyrocatechol. In special experiments, we found that resorcinol does not form complexes with copper in alkaline media.

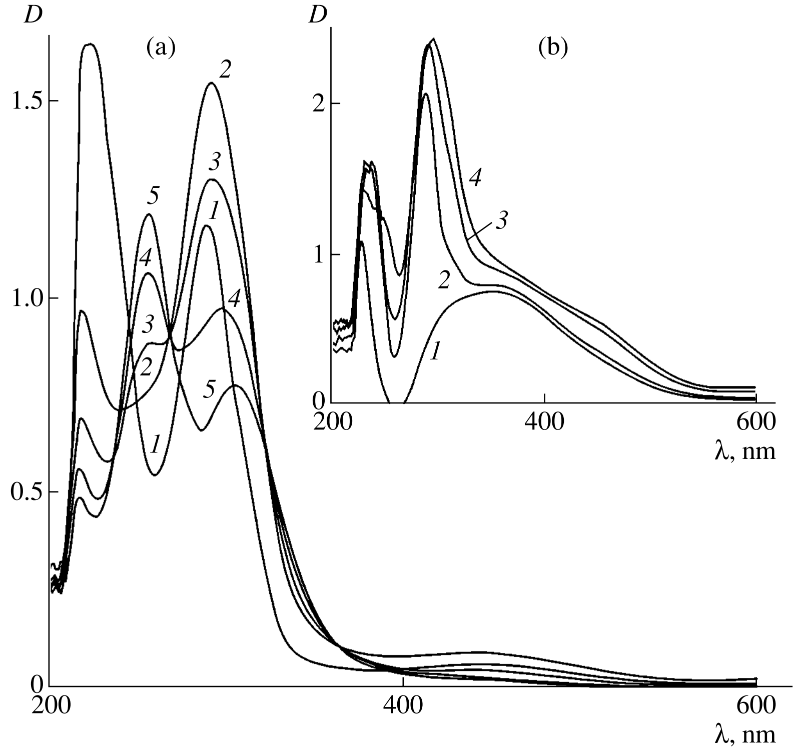


Fig. 6. Changes in the absorption spectra of the reaction mixtures on resorcinol oxidation with time: 1×10^{-3} M $Cu(OH)_2$; 0.5 wt % starch; 0.05 M NaOH; 1×10^{-3} M resorcinol; and (a) 0.01 or (b) 0.025 M H_2O_2. Reaction times, min: (*1*) 1, (*2*) 3, (*3*) 5, (*4*) 10, and (*5*) 15. Reference solution: colloid $Cu(OH)_2$ without resorcinol and H_2O_2, $l = 0.2$ cm.

On the addition of H_2O_2, the above band at 290 nm was observed; however, in this case, the molar absorption coefficient was much higher, and it increased up to 10000 l $mol^{-1}cm^{-1}$ with time (Fig. 6a). This process was concurrent with induction periods in the kinetic curves of H_2O_2 consumption. After the induction period, the concentration of hydrogen peroxide decreased and the product that absorbs at 250 nm was formed, as was observed previously for pyrocatechol [6]. We believe that the lactone that was also formed in pyrocatechol oxidation absorbs at 250 nm; this was supported by the results obtained by liquid chromatography. Direct evidence would be the isolation of the product of resorcinol oxidation. However, low reaction rates and low resorcinol conversions did not allow us to do this.

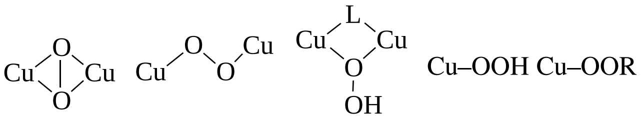
It is believed that a reaction intermediate of resorcinol oxidation absorbs at 290 nm. An isosbestic point at 270 nm suggests that the product of resorcinol oxidation is formed directly from this intermediate. At a higher concentration of H_2O_2, when the catalyst contained a greater amount of peroxides that absorb at 360 and 440 nm (Fig. 6b), oxidation did not occur for a long time, and it began only after the decomposition of a considerable portion of these peroxides.

In a 0.01 M H_2O_2 solution in the presence of 0.03 M NH_3, the oxidation of resorcinol was accelerated so that the product was almost completely formed in the first minutes of the reaction. The intermediate that absorbs at 290 nm was not observed, as distinct from the process presented in Fig. 6. In a 0.05 M H_2O_2 solution with ammonia additives, the reaction of hydrogen peroxide decomposition was predominant, whereas the oxidation of the substrate occurred to an insignificant extent.

Colloid particle size. The SAXS data indicate that particles ~30 Å in diameter were primarily formed in the presence of starch in a concentration range of 0.25–2% in colloidal $Cu(OH)_2$ (Fig. 7), although particles with greater diameters (80–90, 120, and 170–180 Å) were also observed. The pronounced discrete particle size distribution is a consequence of the nature of the hydroxide: coarse particles are formed by the association of small particles; therefore, the diameters of coarse particles are approximate multiples of 30. A decrease in the concentration of copper by a factor of only 2 decreased the number of coarse particles (Fig. 7). The addition of ammonia and an increase in the concentration of starch had the same effect. Note that, in the presence of H_2O_2, in contrast to the effects of other components of the reaction mixture, the ratio between particles of different sizes does not change, but rather the diameter of particles increases (Fig. 7).

DISCUSSION

By now, a number of structurally different peroxo complexes of copper have been synthesized and characterized:



I **II** **III** **IV** **V**

Compounds **I** are considered as structural models of hemocyanin and tyrosinase, which have two closely spaced copper ions in their active centers. Compounds **IV** are considered as models of the enzyme dopamine monoxygenase, which also contains two copper ions, but they are widely spaced (by more than 7 Å). The main principle of the synthesis of these peroxo complexes consists in the attachment of molecular O_2 to Cu(I) complexes or in the attachment of H_2O_2 to Cu(II) complexes.

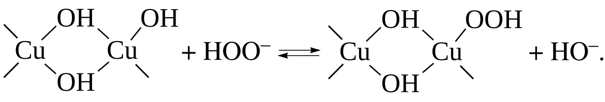
Copper complexes with sophisticated polydentate ligands are used as starting compounds for the synthesis of peroxides; however, the synthesis of the ligands is an independent challenge [13]. The resulting peroxides only dissolve in organic solvents; in the majority of cases, they exist at temperatures of no higher than –40°C. As a rule, experimental studies of their reactivity are difficult to perform because the inherent active oxygen of peroxides more frequently reacts with the ligands rather than with an external substrate. For this reason, the interaction with O_2 or H_2O_2 often results in complexes with oxidized ligands rather than in peroxides.

In this context, copper hydroxide can be considered as a catalyst with unique properties. First, it has the simplest composition because it contains no ligands other than water and its fragments. Second, it readily forms peroxo complexes, which can occur in aqueous solutions, at room temperature. Third, the formation of a number of peroxides (designated as P_{280}, P_{360}, and P_{440}) rather than a single peroxide provides an opportunity to study equilibria between them. Finally, the results of this work allow us to reveal a peroxo complex that is most active under the conditions described.

Previously [4], based on a study of the kinetics of H_2O_2 decomposition in the presence of colloidal and supported copper hydroxides, we proposed a scheme of this reaction. Here, we repeat it taking into account the new results.

The copper hydroxide molecule has a polymeric structure, which consists of square-planar chains [14]. The simplest reaction pathway of the formation of a peroxo complex is the attachment of H_2O_2 to terminal copper ions with the formation of a terminal peroxide:

$$\mathrm{HOOH} \rightleftharpoons \mathrm{HOO^-} + \mathrm{H^+}, \qquad \text{(I)}$$



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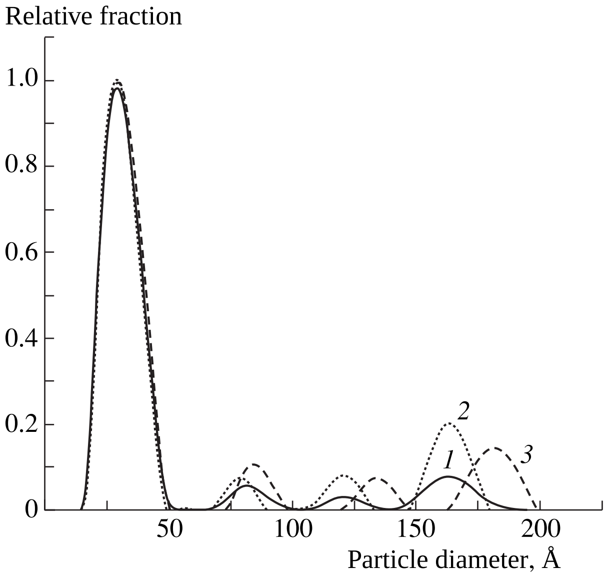
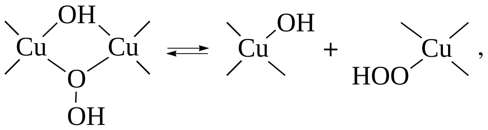
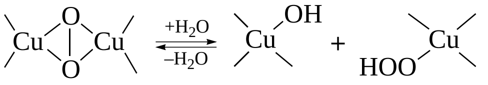


Fig. 7. Particle size distribution in colloid $Cu(OH)_2$ stabilized with 0.5 wt % starch in 0.01 M NaOH: (*1*) 1×10^{-3} M $[Cu(OH)_2]$, (*2*) 2×10^{-3} M $[Cu(OH)_2]$, and (*3*) 1×10^{-3} M $[Cu(OH)_2]$ in the presence of 0.05 M H_2O_2.

We believe that the peroxide that absorbs at 280 nm is formed by this pathway. Moreover, it can be formed by the decomposition of binuclear peroxides:



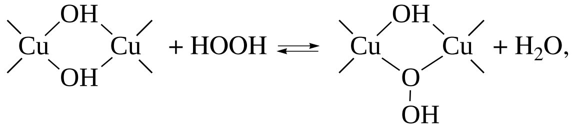
(III)

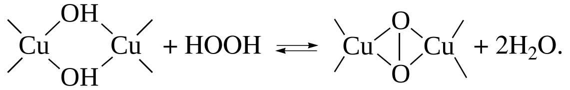


(IV)

For this reason, the concentration of P_{280} changed only slightly when bridging peroxides began to decompose (Fig. 2).

On the other hand, bridging peroxo complexes are formed in reverse reactions (III) and (IV) analogously to the production of binuclear peroxides with organic ligands [1, 2]. This “cross-linking” through terminal groups explains the increase in the size of colloid particles after the addition of H_2O_2. Evidently, the higher the concentration of copper, the higher the possibility of formation of bridging complexes and the higher their concentration. We observed this behavior with the use of SAXS data and absorption spectra as the concentration of $Cu(OH)_2$ was changed from 1×10^{-3} to 2×10^{-3} M. Another reaction pathway of the formation of bridging peroxides through direct interaction with bridging hydroxyl groups, which is also used in the synthesis of complexes with organic ligands, also cannot be excluded:


(V)


(VI)

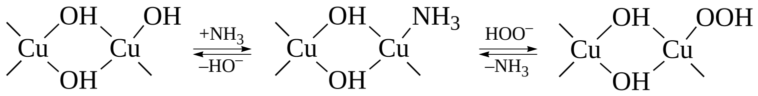
Equilibria (I) and (II) explain the effect of the alkalinity of solutions. On the one hand, an increase in the concentration of NaOH shifts equilibrium (I) to the right; however, on the other hand, OH^- and OOH^- begin to compete for places in the coordination spheres of copper ions. Because of this, the reaction rate of H_2O_2 decomposition is an extremal function of the concentration of NaOH (Table 1).

The position of the absorption band maximum of a peroxide at 360 nm almost coincides with that for complexes **I** [1, 12, 15]. Complexes **II** absorb at ~500 nm, whereas complexes **III** absorb near 400 nm [1, 12, 16]. Therefore, we believe that P_{440} most likely exhibits structure **III**. This structural assignment was supported by the behavior of the test peroxides. Chen *et al.* [11] reported the force constants $F_{Cu–O}$, which characterize the strength of the Cu–OO bond, for different structures:

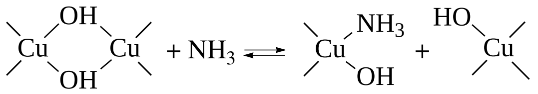
$F_{Cu–O}$, mdyn/Å	1.54	1.03	2.94	3.03
Structure	**I**	**III**	**IV**	**V**

In complete agreement with this order, we observed the highest rate of decomposition in peroxide P_{440}, whereas P_{280} could be detected in small amounts in working solutions (without ammonia additives) even after two days. Recall that the relative concentration of P_{360} increased with NaOH concentration in the reaction mixture; this is consistent with fully deprotonated structure **I**. Although the above spectroscopic data were obtained for copper complexes with other ligand environments, we believe that the relative positions of bands and the orders of stability were also retained on a qualitative level in the case of $Cu(OH)_2$.

At low ammonia concentrations, additional equilibria appeared as follows:


(VII)

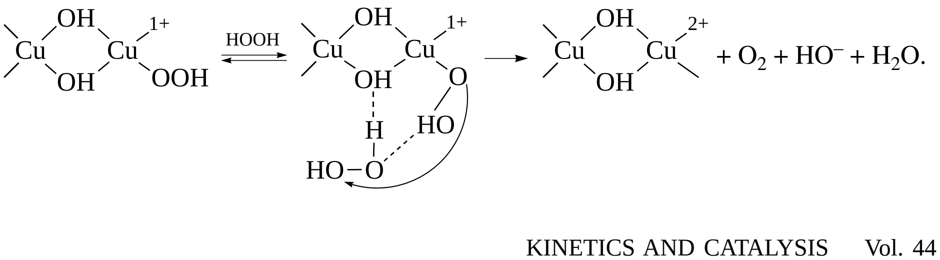
For this reason, the concentration of P_{280} was lower than that in the absence of NH_3; that is, a time is required for its accumulation (Fig. 4, curve *1*). Moreover, equilibrium (VII) also explains why P_{280} disappeared more rapidly in the presence of ammonia than in the absence of it. Large additives of NH_3 can disrupt bridging bonds in $Cu(OH)_2$ to decrease the size of polymer hydroxide molecules and to create additional terminal copper ions:


(VIII)

It is evident that the greater the number of terminal groups, the higher the concentrations of not only P_{280} but also bridging peroxides because of reverse reactions (III) and (IV), as observed experimentally (Table 2).

The set of results suggests that a terminal peroxide is active in the reaction of H_2O_2 decomposition. This is evident from the following: (a) an acceleration of the reaction in the presence of not only ammonia but also other ligands that are capable of breaking hydroxyl bridges between copper ions (bipyridyl, phenanthroline, and pyrophosphate [4]) and thereby producing new terminal groups; (b) the appearance of induction periods in the kinetic curves of H_2O_2 decomposition, which correspond to the accumulation time of P_{280}; (c) a correlation (in the majority of cases) between the concentration of P_{280} and the rate of H_2O_2 decomposition; and (d) an inhibition of the reaction on the repeated addition of H_2O_2 to the reaction mixture when the major portion of the catalyst was bound in bridging peroxides [4].

The second oxidant molecule, which is required for the formation of O_2, does not enter the first coordination sphere but is retained near the reaction site, for example, by hydrogen bonds [4]:

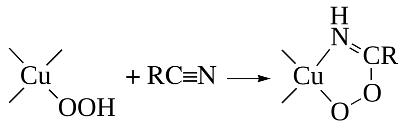

(IX)

The formation of hydrogen bonds is not a necessary condition for H_2O_2 decomposition. We regard this process as only one of the ways in which the reacting molecular entities approach each other, although other possibilities for this can also occur in a complex polymer catalyst, such as a hydroxide [4].

We believe that a scheme analogous to (IX) is also valid for other reactions that occur in the test systems. A terminally coordinated peroxide is catalytically active, and a substrate reacts with it from the second coordination sphere of an active center:

$$\mathrm{Cu{-}OOH} + \mathrm{S} \longrightarrow \{\mathrm{Cu{-}OOH}\cdot\cdot\mathrm{S}\} \longrightarrow \mathrm{Cu{-}OOSH}. \quad \text{(X)}$$

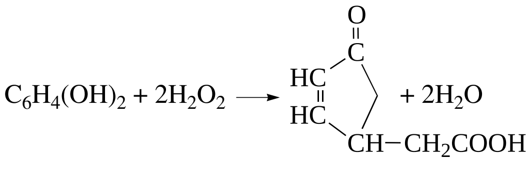
The structure and composition of the obtained intermediate of the reaction of benzonitrile with H_2O_2 in the presence of $Cu(OH)_2$ are evidence in favor of this assumption. The formation of this intermediate can be represented by the reaction



(XI)

Note that, according to EPR data and electronic spectra, copper hydroxide does not form complexes with nitriles in the absence of H_2O_2. Nitriles react with H_2O_2 to form peroxyimidic acids in alkaline media and in the absence of catalysts [17]. Therefore, we may assumed that a pink complex is formed in the ordinary way: a peroxyimidic acid is formed in solution; then, it coordinates to the catalyst. In this case, the more peroxide added, the higher the concentrations of both the peroxyimidic acid and its complex with the catalyst. However, we observed a decrease in the concentration of the pink intermediate with increasing H_2O_2 content. This intermediate was not formed at all, as the concentration of the catalyst was increased, when terminal peroxo ligands were converted into bridging ligands. Consequently, terminal peroxo ligands are required for the formation of the pink complex. Moreover, if the reaction occurred in the ordinary way, weakly bound bridging peroxides could not be a hindrance to the coordination of a bidentate peroxyimidic acid. This is particularly important if we remember the considerable effect of a weak ligand such as ammonia on all equilibria between the catalyst and H_2O_2. Because of this, we believe that a coordinated peroxyimidic acid is formed in reaction (XI). There is a good probability that it is formed on the catalyst more rapidly than in solution.

The oxidation of diphenols to a hydromuconic acid lactone occurs by the reaction



(XII)

As distinct from pyrocatechol, which is a bidentate ligand of great coordinating ability, resorcinol does not form complexes with copper in neutral and alkaline media. Nevertheless, both of the diphenols react via identical (or very similar) intermediates. This can take place only in the case when a substrate that does not enter the first coordination sphere of an active center directly reacts with a coordinated oxidizing agent in accordance with scheme (X). Interactions of this type were supported by an acceleration of the reaction of resorcinol oxidation in the presence of added ammonia, which is favorable for the formation of terminal Cu–OOH groups, and by an inhibition of the oxidation on the catalyst, which is bound in bridging peroxides to a considerable extent. We are also reminded that the pink intermediate was not formed in the reaction with nitriles under conditions favorable for the formation of bridging peroxides on the catalyst (at high hydroxide and (or) H_2O_2 concentrations).

Thus, in this work, we found that a terminal peroxide participates in the nonradical mechanism of the catalytic decomposition of H_2O_2 and the oxidation of substrates in the presence of copper hydroxide. In this case, even substrates that exhibit a chelating ability (pyrocatechol) react with the coordinated oxidant from the second rather than first coordination sphere of an active center.

Note that the absence of catalytic activity toward bridging peroxide formation does not imply that they are completely unreactive. It is most likely that a terminal peroxide acts as a nucleophilic agent, whereas bridging peroxides exhibit sufficiently strong electrophilic reactivity [2, 12]. This may be of importance for the activation of saturated molecules, such as saturated hydrocarbons, which possess very weak reducing and coordinating properties and in which the outer-sphere interaction with a coordinated oxidant is most probable.

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