

# The Role of Peroxo Complexes in the Catalytic Decomposition of $\text{H}_2\text{O}_2$ in the Presence of Cu(II) Hydroxides

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**Abstract**—The catalytic decomposition of hydrogen peroxide is studied in the presence of colloidal and silica-gel-supported  $\text{Cu}(\text{OH})_2$ . Copper peroxy complexes with different activities were identified. The reaction is molecular without radical formation. The mechanisms of  $\text{H}_2\text{O}_2$  decomposition are discussed.

## INTRODUCTION

Natural enzymes, such as oxide reductase, are excellent catalysts for many oxidative reactions in aqueous solutions. Therefore, considerable efforts are made to elucidate their structure and determine how their prosthetic centers work. For instance, the catalytic cycle of the non-heme enzymes tyrosinase and laccase, which have polynuclear copper-containing active centers, involves the formation of intermediate peroxy complexes. To elucidate the nature of these peroxydes, several dozens of copper complexes with complex organic ligands were synthesized [1]. Few of them form peroxy compounds in reactions with  $\text{O}_2$  or  $\text{H}_2\text{O}_2$ . The data on the structure of synthetic peroxydes provide insights into the structure of enzymes [2]. Thus, most of researchers' efforts are directed toward the design of structural rather than functional analogs of natural catalysts.

This article deals with the interaction of colloidal and silica-gel-supported  $\text{Cu}(\text{OH})_2$  with hydrogen peroxide in the catalytic composition of this substance. These relatively simple systems form copper peroxy complexes which are identifiable by spectrophotometry.

## EXPERIMENTAL

The following reagents were used in this study:  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ , bipyridine (bpy), phenanthroline (phen), pyridine (py),  $\beta$ -naphthol, di(*t*-butyl)phenol (all analytical purity grade), water-soluble starch for iodometry; and  $\text{SiO}_2$  (KSKG trademark, Dzerzhinsk) with a specific surface area of  $300 \text{ m}^2/\text{g}$ . All solutions were prepared in doubly distilled water.

Solutions and catalysts were analyzed for  $\text{H}_2\text{O}_2$  by titration with  $\text{Ce}(\text{IV})$  or by the formation of a yellow complex with  $\text{Ti}(\text{IV})$  [3]. The concentration of copper was determined by biquinoline [3].

The absorption spectra of colloidal solutions and diffuse-reflectance spectra of solid samples were registered on UV 300 (Shimadzu) and M-40 (Carl Zeiss Jena) spectrophotometers, respectively. The values of

pH were measured by an ion-meter I-135. Low oxygen concentrations ( $<2 \times 10^{-4} \text{ mol/l}$ ) were determined using a Beckman Monitor II with the Clark electrode.

Reaction kinetics was studied by  $\text{O}_2$  formation in a volumetric setup at a temperature of 298 K, which was kept constant, or by changes in  $\text{H}_2\text{O}_2$  concentration in a solution (reaction with  $\text{Ti}(\text{IV})$ ). Initial pH was set by adding  $\text{HNO}_3$  and  $\text{NaOH}$  for kinetic measurements.

$\text{Cu}(\text{OH})_2$  stabilized by starch was synthesized by dissolving 0.5 g of starch in 100 ml of hot water, adding 1.3–6.5 ml of copper nitrate (0.078 M) solution to the cooled solution, and stirring while adding 0.5 M of  $\text{NaOH}$  to pH 10–11. The resulting colloidal solutions were transparent and suitable for spectrophotometric studies. They contained 0.001–0.005 mol/l of  $\text{Cu}(\text{OH})_2$  in a 0.5 wt % solution of starch.

Synthesis of  $\text{Cu}(\text{OH})_2$  supported on  $\text{SiO}_2$  containing 2 wt % of copper was described in [4].

## RESULTS

The  $\text{Cu}(\text{II})$  ions are hydrolyzed at  $\text{pH} > 6$ . Therefore, kinetic measurements were carried out at higher pH to prevent dissolution of colloidal  $\text{Cu}(\text{OH})_2$  and washing supported  $\text{Cu}(\text{OH})_2$  out.

### Catalytic Properties of Colloidal $\text{Cu}(\text{OH})_2$

The preparation procedure of colloidal  $\text{Cu}(\text{OH})_2$  stabilized by starch makes it possible to obtain transparent solutions which are stable for several days and do not form copper hydroxide or oxide precipitate.

The table shows the rates of  $\text{O}_2$  formation at the initial segment of kinetic curves for  $\text{H}_2\text{O}_2$  decomposition in the colloidal solutions of  $\text{Cu}(\text{OH})_2$  in the presence of additives. The results of kinetic measurements were the same independently of the method ( $\text{H}_2\text{O}_2$  and  $\text{O}_2$ ) used. This points to the absence of the side process of starch oxidation. The kinetic curves become linear in the  $\log[\text{H}_2\text{O}_2]_t - t$  coordinates pointing to the first-order reaction kinetics.

Initial rates of  $O_2$  formation ( $w_0$ ) in  $H_2O_2$  decomposition in the colloidal solution of  $Cu(OH)_2$  in the absence and presence of additives (L)\*

L	L : Cu, mol/mol	$w_0$ , ml $O_2$ /min	L	L : Cu, mol/mol	$w_0$ , ml $O_2$ /min
—	—	0.5	bpy; $\beta$ -naphthol	0.4; 0.3	5.7
$\beta$ -naphthol	0.3	0.5	phen	1.0	6.9
bpy	0.4	5.9	py	3.0	0.6
"	1.0	6.8	"	5.0	0.4
"	2.0	5.9	$P_2O_7^{4-}$	20.0	1.9

\*  $[Cu(OH)_2] = 1 \times 10^{-3}$  mol/l,  $[H_2O_2] = 0.05$  mol/l, 0.5 wt % of starch, 25 ml of solution, and pH 10.5.

### Effect of Additives on Reaction Kinetics

**Alcohols.** The formation of free radicals in the catalytic decomposition of  $H_2O_2$  is usually determined by the inhibitor method, that is, by adding radical acceptors to working solutions. Such acceptors can be alcohols, *p*-nitrosodimethylaniline (PNDMA), or others [5]. If free radicals are present, the kinetic curves of  $O_2$  consumption has an induction period and become *S*-shaped. In our experiments,  $\beta$ -naphthol or di(*t*-butyl)phenol additives ( $5 \times 10^{-5}$ – $5 \times 10^{-4}$  mol/l) did not result in a decrease in the reaction rate and did not change the form of kinetic curves. This fact suggests that  $H_2O_2$  decomposition in the presence of  $Cu(OH)_2$  is molecular. Lunenok-Burmakina *et al.* [6] came to the same conclusion when they studied  $H_2O_2$  decomposition in alkali solutions of  $CuSO_4$  and a PNDMA inhibitor.

**Nitrogen-containing ligands.** The addition of bpy, phen, dimethylphenanthroline, or similar ligands ( $L : Cu = 0.4$ ) resulted in a multiple increase in the reaction rate (see the table). If ligands are added in amounts higher than equimolar with respect to copper, the reaction rate and the  $O_2$  yield decrease. The presence of  $\beta$ -naphthol together with bpy had no effect on the reaction kinetics. Pyridine additives do not affect the reaction rate up to reaching a py : Cu ratio of 3, after which the reaction is somewhat retarded.

**Pyrophosphate ions.** To maintain constant pH in the reaction mixture, we tried to use a pyrophosphate buffer characterized by a high capacity at pH 6–11. We found that  $H_2O_2$  decomposition is substantially retarded in an 0.02 M solution of this buffer at pH < 9.  $\beta$ -Naphthol additives change the usual kinetic curve to *S*-shaped. Thus, in the presence of pyrophosphate ions at pH 7–9, the reaction mechanism involves radicals. At pH > 9, the reaction rate is higher in the pyrophosphate buffer than without it (see the table), and the presence of  $\beta$ -naphthol does not affect the kinetics of  $H_2O_2$  decomposition.

**Hydroxyl ions.** When  $H_2O_2$  is added to colloidal  $Cu(OH)_2$ , the reaction mixture becomes much more acidic. If  $H_2O_2$  is added in a concentration of 0.05 mol/l to colloidal  $Cu(OH)_2$  with pH 11, the pH immediately decreases to 10.5–10.6. If the concentration of  $H_2O_2$  is 0.3 mol/l, the pH drops to 10.1–10.2. Then, in the

course of the catalytic decomposition of  $H_2O_2$ , the reaction mixture becomes more basic and the pH almost returns to its initial value before  $H_2O_2$  addition. The overall process is electroneutral as agrees with its stoichiometry. This makes it difficult to study the effect of pH on kinetics. The use of buffers is incorrect because all buffers known to us possess complex-forming properties and may affect the rate and mechanism of the process as pyrophosphate does. Therefore, to study the effect of  $OH^-$  concentration, we used the following technique: 0.1 mol/l of  $H_2O_2$  was added to  $1 \times 10^{-3}$  M colloidal  $Cu(OH)_2$  with pH 8.5. The value of pH decreased to 7.0–7.1. Then, the exact volumes of 0.5 M NaOH were added to the reaction mixture and the kinetic curve of  $O_2$  evolution was registered.

Figure 1 shows the dependence of the initial rate on the concentration of added alkali. In separate experiments, we found that the series of NaOH concentrations corresponds to pH 7–11. Figure 1 (curve 1) shows that, at 0.1 mol/l  $H_2O_2$ , the reaction rate depends on  $[OH^-]$  only when the concentration of  $OH^-$  is low (pH 7–8). A similar curve with a plateau is observed for the dependence of initial rates on the concentration of  $OH^-$  at  $[H_2O_2] = 0.5$  mol/l.

### Dependence of the Reaction on the $H_2O_2$ Concentration

We already noted that, upon adding the different amounts of  $H_2O_2$  to the reaction mixture, different pH are set. To preserve at least the initial values of pH after adding  $H_2O_2$ , the pH of the reaction mixture was adjusted to 10–11 by adding NaOH. It was found that, at  $[H_2O_2] = 0.01$ – $0.2$  mol/l, the reaction order with respect to  $H_2O_2$  is close to 0.5. At  $[H_2O_2] = 0.2$ – $1.0$  mol/l, the rate does not depend on the  $H_2O_2$  concentration (Fig. 1, curve 2).

### Dependence of the Reaction on the Catalyst Concentration

This dependence was studied as follows: a colloidal solution containing  $5 \times 10^{-3}$  mol/l  $Cu(OH)_2$  in 0.5% starch was prepared (more concentrated colloids are unstable) at pH 10. Then, this solution was diluted by a similar solution of starch to the desired concentration of the catalyst. At  $[Cu(OH)_2] = 5 \times 10^{-4}$ – $5 \times 10^{-3}$  mol/l,

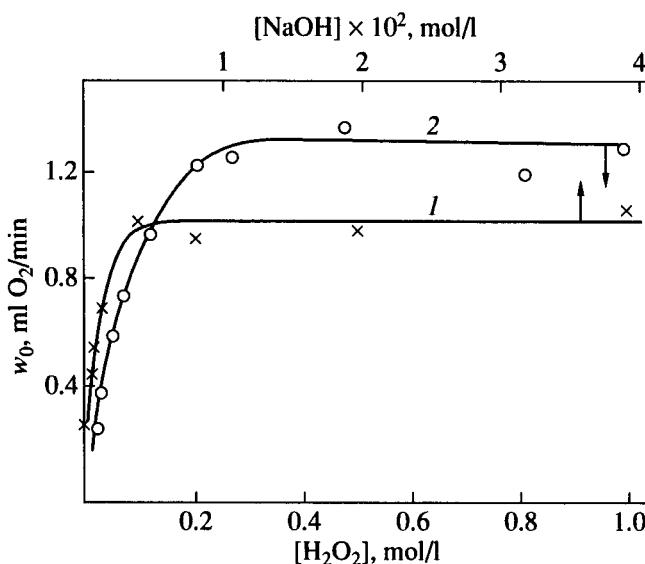


Fig. 1. Dependence of the initial rate  $w_0$  of  $\text{H}_2\text{O}_2$  decomposition on the concentration of (1)  $\text{NaOH}$  and (2)  $\text{H}_2\text{O}_2$  in the colloidal solutions of  $\text{Cu}(\text{OH})_2$  stabilized by starch: (1)  $[\text{Cu}(\text{OH})_2] = 1 \times 10^{-3} \text{ mol/l}$ ; (2)  $[\text{H}_2\text{O}_2] = 0.1 \text{ mol/l}$ , pH 10–11; the volume of solution is 25 ml.

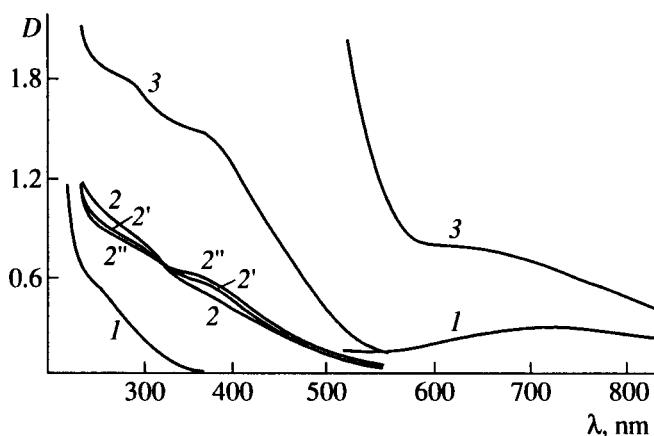


Fig. 2. Spectra of colloidal  $\text{Cu}(\text{OH})_2$  solutions stabilized by starch in the (1) absence and (2, 3) presence of  $\text{H}_2\text{O}_2$  at pH 10: (1)  $[\text{Cu}(\text{OH})_2] = 1 \times 10^{-3} \text{ mol/l}$ ; (2)  $[\text{H}_2\text{O}_2] = 0.01 \text{ mol/l}$ ; (3)  $[\text{H}_2\text{O}_2] = 0.1 \text{ mol/l}$ . Reaction lasted (2) 0, (2') 5, and (2'') 10. The length of a cell is 0.1 (for  $< 500 \text{ nm}$ ) or 5 cm (for  $> 500 \text{ nm}$ ).

the reaction order of 0.1 M  $\text{H}_2\text{O}_2$  solution decomposition with respect to the catalyst is 1.1.

#### Colloid Absorption Spectra

Colloidal solutions of  $\text{Cu}(\text{OH})_2$  at pH 7–11 have absorption bands at 250 ( $\epsilon = 2500 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) and 720 nm ( $\epsilon = 40 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) (Fig. 2, curve 1). When we add 0.01 mol/l  $\text{H}_2\text{O}_2$ , new bands appear at 280 and 350 nm independently of pH, and the intensity of the absorption substantially increases in the entire spectrum. (Fig. 2, curve 2). For several minutes after adding

$\text{H}_2\text{O}_2$ , the absorbance at 280 nm decreases and the absorbance at 350 nm increases (curves 2, 2', and 2''). At  $[\text{H}_2\text{O}_2] \geq 0.1 \text{ mol/l}$ , the spectrum has the form of curve 3 and does not change until reaction completion.

When we add bpy to the colloidal solution of  $\text{Cu}(\text{OH})_2$  in the 1 : 1 ratio, the  $d-d$  transition band of the  $\text{Cu}^{2+}$  ion shifts from 720 to 650 nm. In the presence of  $\text{H}_2\text{O}_2$  ( $\geq 0.05 \text{ mol/l}$ ), the above-mentioned bands at 280 and 350 nm appear in the spectrum. Their intensity is very low and they completely disappear upon reaction completion. The same effects are observed in the pyrophosphate buffer (0.02 M, pH 10). The spectrum of a solution with  $\text{py} : \text{Cu} = 3$  after adding  $\text{H}_2\text{O}_2$  remains virtually the same as in the absence of py both in the beginning and at the end of the reaction.

#### Peroxo Complex Decomposition

When  $\text{H}_2\text{O}_2$  decomposition is completed, complexes that were formed in the presence of  $\text{H}_2\text{O}_2$  start to disappear. Figure 3 (curve 1) shows a decrease in the absorbance at 350 nm (pH increases from 10.4 to 10.9), which is observed after the completion of  $\text{O}_2$  evolution monitored by the volumetric method. According to chemical analyses, the beginning of this curve corresponds to a  $\text{H}_2\text{O}_2 : \text{Cu}$  ratio of 0.6–0.7. After 2 h, this ratio decreases to ~0.2 and then remains unchanged for a day. Hydrogen peroxide disappears from the solution after several days, and the spectrum becomes identical to that of the initial colloidal  $\text{Cu}(\text{OH})_2$ . Unlike the kinetic curve for the process of  $\text{H}_2\text{O}_2$  decomposition, the curve for peroxy complex decomposition (Fig. 3, curve 1) is linearized in the  $1/C_r - t$  coordinates. This corresponds to the second-order reaction kinetics. In our calculations, we assumed that the absorbance  $D_{350}$  is proportional to the complex concentration.

A decrease in the intensity of absorption at 350 nm is accompanied by oxygen evolution registered by the Clark electrode (Fig. 3, curve 1'). Simultaneously, the bands for the initial colloid (250 and 720 nm) appear and become more intense. These processes are 2–3 times slower in the neutral medium than in the alkali medium.

The rate of peroxy complex decomposition does not change in the presence of pyridine (Fig. 3, curve 2). The additives of pyrophosphate (or bpy) accelerate this process (Fig. 3, curve 3) and increase the amount of oxygen evolved (curve 3') due to the deeper decomposition of peroxydes (compare curves 1 and 3).

#### Catalytic Properties of $\text{Cu}(\text{OH})_2$ Supported on $\text{SiO}_2$

The diffuse-reflectance spectrum of  $\text{Cu}(\text{OH})_2/\text{SiO}_2$  completely coincides with the spectrum of bulk  $\text{Cu}(\text{OH})_2$  and confirms the hydroxide nature of the supported catalysts. Upon reacting with  $\text{H}_2\text{O}_2$ , the spectra of filtered samples have an intense band at 360–380 nm, which corresponds to the formation of peroxy complexes.

We determined the  $\text{H}_2\text{O}_2 : \text{Cu}$  molar ratio in supported samples after  $\text{H}_2\text{O}_2$  decomposition at different pH,  $\text{H}_2\text{O}_2$  concentrations, and catalyst loadings. Figure 4 shows the results suggesting that the amount of hydrogen peroxide coordinated by the catalyst decreases and then reaches a constant value as pH increases from 6 to 7–8. The  $\text{H}_2\text{O}_2 : \text{Cu}$  ratio in the catalyst increases with an increase in the concentration of hydrogen peroxide as  $\text{H}_2\text{O}_2$  excess over the catalyst loading becomes more pronounced.

To determine the maximal  $\text{H}_2\text{O}_2 : \text{Cu}$  ratio, we added 10 ml of  $\text{H}_2\text{O}_2$  solutions (with concentrations of 2.0, 4.0, and 10.0 mol/l) at pH 6.5 to 0.2 g of the catalyst and stirred for 30 min. The resulting mixture was carried over to the filter. The precipitate was thoroughly washed with water to remove excess  $\text{H}_2\text{O}_2$ . This was checked by the absence of the reaction of flush water with Ti(IV). Then, the precipitate was analyzed without drying. In the resulting samples, the  $\text{H}_2\text{O}_2 : \text{Cu}$  ratio remained constant (0.5), suggesting that only one complex is formed under these conditions. This complex has two copper ions per one hydrogen peroxide molecule. In the case of the supported samples, several peroxy complexes are probably formed, but after long procedures of sample preparation for analysis, only one complex remains, which is the most stable. In further use of these samples in  $\text{H}_2\text{O}_2$  decomposition, the reaction rate substantially decreases as compared to the rate on the fresh catalysts. These facts suggest that the most stable peroxy complex is inactive.

The peroxy complex of supported  $\text{Cu}(\text{OH})_2$  (as in the case of the colloidal  $\text{Cu}(\text{OH})_2$ ) gradually decomposes, as is evident from a decrease in the band intensity at 360–380 nm upon sample storage. However, by contrast to colloidal samples, this process is much slower in solid catalysts: hydrogen peroxide is preserved in noticeable amounts even after storing the sample for a month.  $\text{Cu}(\text{OH})_2$  without additional ligands is accumulated in the samples (the intensity of a band at 720 nm increases).

For supported samples, we managed to trace the effect of the concentration of the inactive peroxy complex in the catalyst on the dependence of the  $\text{H}_2\text{O}_2$  decomposition rate on the concentration of  $\text{H}_2\text{O}_2$  and pH. The reaction rate increases at pH 6–8 and then remains constant at pH 8–13 (Fig. 5, curve 1). This dependence corresponds to a decrease and further constancy of the inactive complex concentration in the sample under the same conditions (cf. curve 1, in Fig. 4). The reaction is first-order in  $\text{H}_2\text{O}_2$  at the concentrations of hydrogen peroxide between 0.01 and 0.1 mol/l (pH 10). Under these conditions, the catalyst does not contain the inactive complex. At higher concentrations of hydrogen peroxide, which are favorable for the accumulation of the inactive complex, the reaction order is lower (Fig. 5, curve 2).

The effect of ligands on the reaction kinetics under the conditions of heterogeneous catalysis is analogous to that observed in the case of a colloidal catalyst. In the

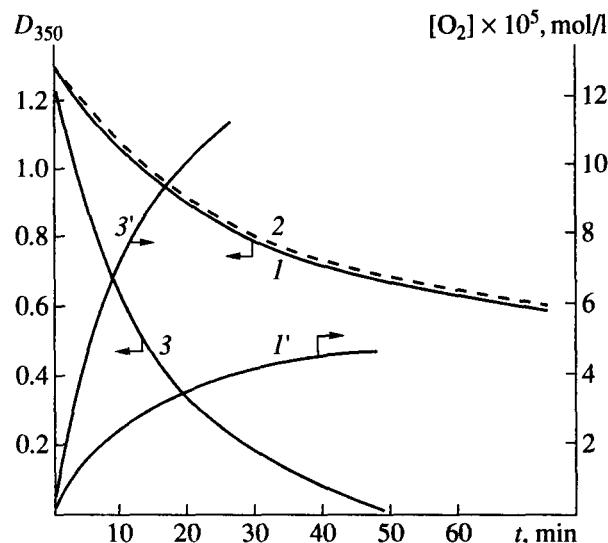


Fig. 3. Absorbance at 350 nm and the corresponding kinetic curves of  $\text{O}_2$  formation upon the completion of  $\text{H}_2\text{O}_2$  decomposition in the colloidal solution of  $\text{Cu}(\text{OH})_2$  at  $\text{pH} \sim 10$ ,  $[\text{H}_2\text{O}_2] = 0.05 \text{ mol/l}$ , and  $[\text{Cu}(\text{OH})_2] = 1 \times 10^{-3} \text{ mol/l}$ : (1, 1')  $D_{350}$  and  $\text{O}_2$  formation,  $\text{pH} 10.4$ – $10.9$ ; (2) the same in the presence of  $3 \times 10^{-3} \text{ mol/l}$  bpy; and (3, 3') the same in the presence of  $1 \times 10^{-2} \text{ mol/l}$   $\text{P}_2\text{O}_7^{4-}$ .

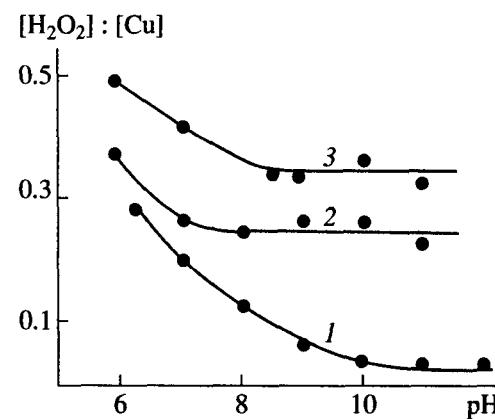


Fig. 4. Dependence of pH on the  $\text{H}_2\text{O}_2 : \text{Cu}$  molar ratio in the  $\text{Cu}(\text{OH})_2/\text{SiO}_2$  catalyst upon the completion of  $\text{H}_2\text{O}_2$  decomposition under different conditions: (1) 0.5 g of the catalyst;  $[\text{H}_2\text{O}_2] = 0.1 \text{ mol/l}$ ; (2) 0.5 g of the catalyst;  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/l}$ ; and (3) 0.2 g of the catalyst;  $[\text{H}_2\text{O}_2] = 0.5 \text{ mol/l}$ ; the volume of working solutions is 10 ml; the values of pH correspond to the beginning of the reaction.

pyrophosphate buffer at  $\text{pH} < 9$ ,  $\text{H}_2\text{O}_2$  decomposition substantially decelerates and probably switches to the radical mechanism because the additives  $\beta$ -naphthol make the kinetic curve S-shaped. At  $\text{pH} > 9$ , the reaction is faster in the buffer medium. In the presence of bpy, the reaction accelerates as the bpy : Cu ratio increases from 0.2 to 1 and then decelerates. Upon reaction completion in the presence of pyrophosphate or bpy, the catalyst does not contain stable peroxy complexes. Therefore, the use of the same catalyst in the second run leads to the same rate of  $\text{H}_2\text{O}_2$  decomposition as that over a fresh catalyst.

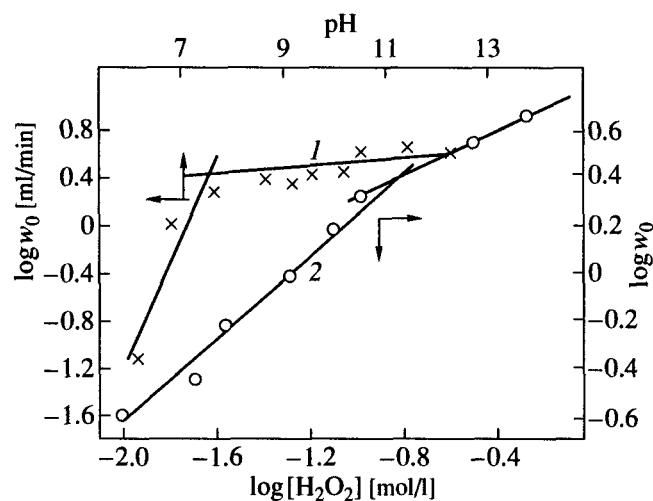
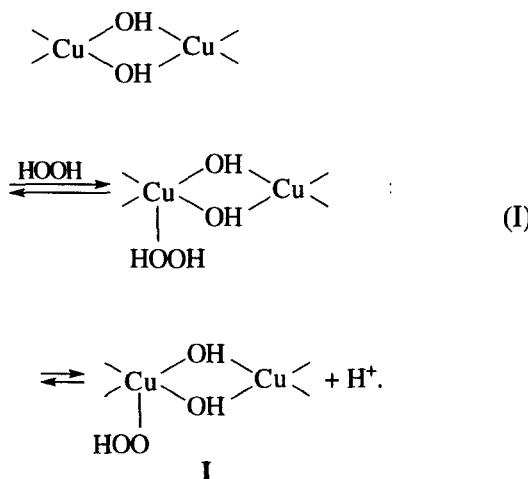


Fig. 5. Dependence of  $\log w_0$  on (1) pH and (2)  $\log[H_2O_2]$  for  $H_2O_2$  decomposition in the presence of  $Cu(OH)_2/SiO_2$ : 0.5 g of the catalyst in 10 ml of solution; (1)  $[H_2O_2] = 0.1 \text{ mol/l}$ ; (2) pH 10–11.

## DISCUSSION

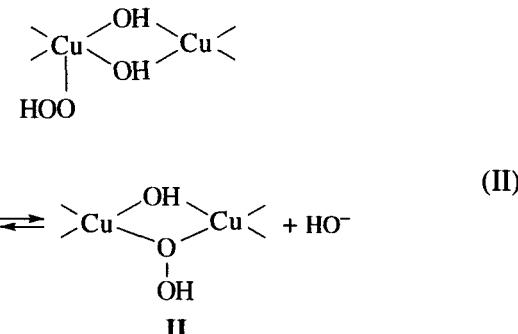
*Mechanism of  $H_2O_2$  decomposition.* Copper hydroxide is a polymeric substance. Copper ions are bridged by hydroxyl groups to form a linear chain [7]. These chains form corrugated layers. That is, this compound is layered, and its structure is completely preserved upon supporting it onto  $SiO_2$  according to our techniques. In the colloidal solution, the polymeric hydroxide molecules are probably rolled into globules protected from sticking together by the shell of a stabilizer (starch). Reacting molecules may enter between layers or inside globules and occupy axial positions in the first coordination shell of copper ions. Therefore, the first step of hydrogen peroxide interaction with the catalyst can be described as peroxide formation via  $H_2O_2$  coordination to the fifth coordination site and proton elimination:



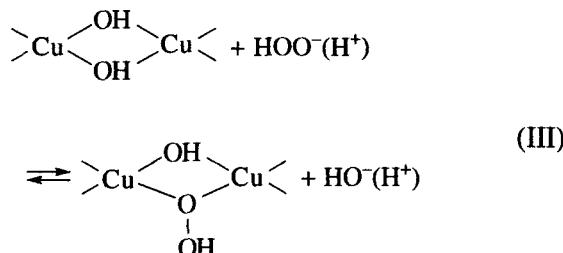
Axial ligands in the copper complexes are usually weakly coordinated (the  $Cu-L$  distance  $r_{Cu-L}$  is longer

than  $2.2 \text{ \AA}$ ) [8]. However, the presence of an adjacent layer in the solid catalyst or polymeric molecule fragments in a globule probably prevents peroxy ligands from stronger binding than on the surface or in solutions of copper ions. This should favor a shift of equilibrium (I) to the right. The following facts point to this equilibrium: (1) the reaction mixture becomes more acidic after the addition of hydrogen peroxide; (2) intensities of absorption bands corresponding to peroxides increase with an increase in the hydrogen peroxide concentration; (3) the dependence of the reaction rate on the hydrogen peroxide concentration has a plateau (Fig. 1).

Another possible coordination mode for  $H_2O_2$  is the occupation of the equatorial position via the substitution of a bridging hydroxyl group by, for example, intramolecular rearrangement of I:



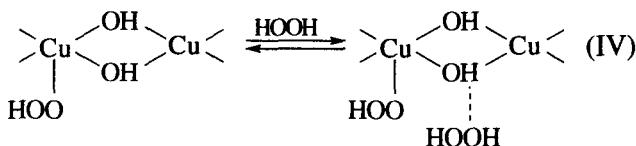
A decrease in the band intensity at  $280 \text{ nm}$  and an increase in the intensity at  $350 \text{ nm}$  in the spectra of colloidal  $Cu(OH)_2$  (Fig. 2, curves 2, 2', and 2'') can be associated with equilibrium (II). Transformation into bridged peroxide II is rather slow if the concentration of  $H_2O_2$  added is low ( $0.01 \text{ mol/l}$ ). At higher concentrations,  $H_2O_2$  and  $OH^-$  compete for the coordination site, and the direct (immediate) substitution of the bridging hydroxyl group becomes possible:



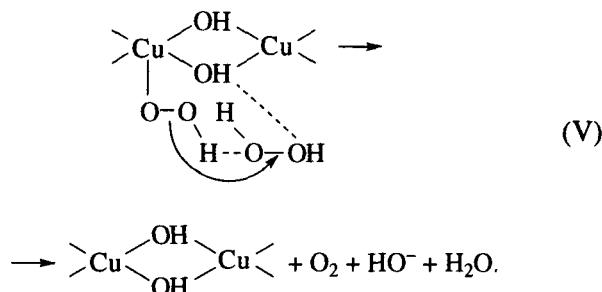
An  $H_2O_2 : Cu$  ratio of 0.5 in supported samples treated by excess  $H_2O_2$  supports the idea that peroxy ligands are coordinated in the bridging positions, and the  $Cu-Cu$  distance  $r_{Cu-Cu}$  is  $2.84 \text{ \AA}$  according to EXAFS (these findings will be reported elsewhere). This agrees well with the structures of a  $\mu$ -1,1 bridge because, for other bridges ( $\mu$ -1,2,  $\mu$ - $\eta^2 : \eta^2$ ), the  $Cu-Cu$  distance is longer than  $3 \text{ \AA}$  [1, 2]. Peroxide II, in which the peroxy group is coordinated in the equatorial position, should be much more thermodynamically stable than complex I. This is a possible explanation for the low activity of II. Equilibria (I) and (II) explain an

increase in the concentration of this peroxide in the catalyst with a decrease in pH and with an increase in excess  $\text{H}_2\text{O}_2$  concentration.

The formation of  $\text{O}_2$  should occur via the reaction of two hydrogen peroxide molecules which are close to each other in the coordination sphere of an active center. We believe that electron transfer between two anions  $\text{HOO}^-$  coordinated in a similar manner to a copper ion or two adjacent copper ions is unlikely because one of the reacting peroxide species should be a stronger oxidant relatively to the other. Electron transfer becomes possible if one of the species is deprotonated and the other is not. Proton abstraction from the molecules of weak acids is favorable when these molecules enter the first coordination shell of metal ions because acid strengthens in this case. Therefore, the second  $\text{H}_2\text{O}_2$  molecule most likely enters the second coordination sphere rather than the first. That is, it forms an outer-sphere complex with copper via, for example, hydrogen bonds:



Then, two differently coordinated peroxide species exchange two electrons to form  $\text{O}_2$  and  $\text{HO}^-$ :

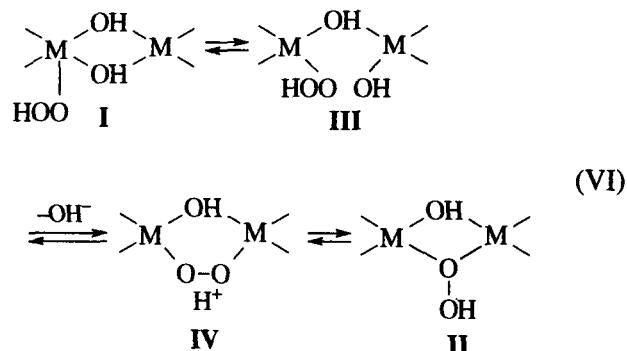


The elimination of  $\text{HO}^-$  in the first step explains the fact that the reaction mixture becomes more basic during the catalytic process.

There is no clear evidence for the rate-determining step in mechanism (I)–(V) for  $\text{H}_2\text{O}_2$  decomposition, but it is highly probable that the formation of  $\text{O}_2$  by step (V), which is not an elementary process, is not rate-determining because the reaction order in  $\text{H}_2\text{O}_2$  is first or lower.

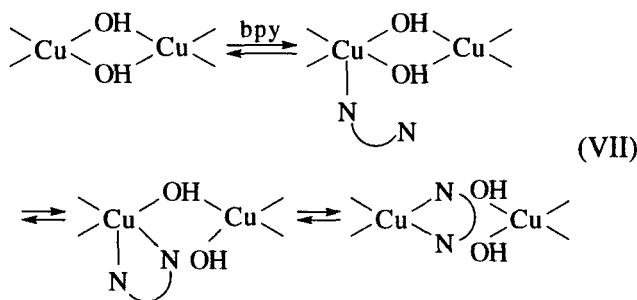
Possibly, a peroxy complex exists that is more active than **I**. This complex might be formed from **I** by structural rearrangement. There are two reasons for such an assumption. First, a short induction period (1–2 min) is sometimes detectable, which is more pronounced at lower pH and  $\text{H}_2\text{O}_2$  concentrations. Second, the region of peroxide **II** absorbance (300–500 nm) is too broad to have only one band. Indeed, the decomposition of spectrum 3 (Fig. 2) into the Gauss components enables the identification of a band at 450 nm along with the bands at 280 and 350 nm. Moreover, the bands

at 250 and 450 nm should be assigned to different complexes because the ratios between the respective absorbances change depending on conditions (pH, the concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Cu}(\text{OH})_2$ , and time elapsed after  $\text{H}_2\text{O}_2$  addition). A number of consecutive transformations of peroxide structures can be described as follows:



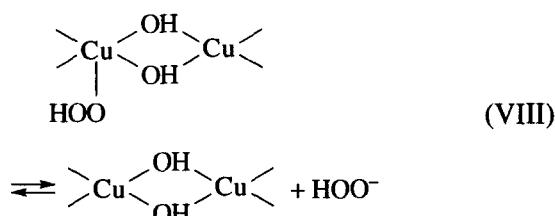
The  $\text{I} \rightarrow \text{III}$  transition is rather probable because the coordination of  $\text{HOO}^-$  in the equatorial position should be stronger than in the axial position. Peroxides **II** and **III** and the equilibria between them are known for copper complexes with organic ligands [9]. Peroxides **II** and **IV** are well studied for cobalt complexes [10]. Thus, it has been found that bridging cobalt peroxides similar to **II** do not react with strong oxidants (preliminary isomerization into **IV** is needed). Peroxide **IV** (that is, *cis*- $\mu$ -1,2 complexes) cannot be oxidized to form oxygen because the use of all oxidants known to date leads to the formation of bridging superoxide by accepting one electron [10, 11]. Possibly, the oxidative elimination of  $\text{O}_2$  from bridged peroxides is hampered in copper complexes. This agrees well with the catalytic properties of peroxide **II**, which we found. Therefore, in the catalytic decomposition of hydrogen peroxide, terminal copper ions in the polymeric  $\text{Cu}(\text{OH})_2$  molecule should be more active than middle ions. The catalytic properties of terminal peroxides **I** and **III** can be different because of different structures and binding strengths to copper ions. This issue is very interesting and should be further studied because we found [12] that, in the systems under study, lower alkanes are oxidized at room temperature and atmospheric pressure. Note also that copper peroxide **II** is discussed as a plausible intermediate in the mechanism of lactase action [2].

*Effect of ligands.* The interaction of ligands with the polymeric  $\text{Cu}(\text{OH})_2$  molecule may follow two pathways described above for  $\text{H}_2\text{O}_2$ : the addition reaction to the fifth coordination site and the substitution of bridging hydroxyls. In the case of bidentate *N*-containing ligands and pyrophosphate which form stable complexes with copper, the polynuclear structure of the catalyst may partially degrade. For example, the following reactions may occur in the case of bpy:

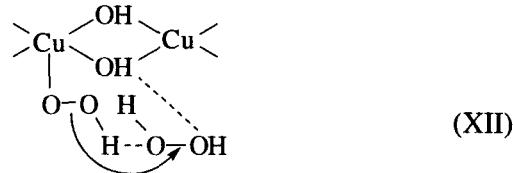
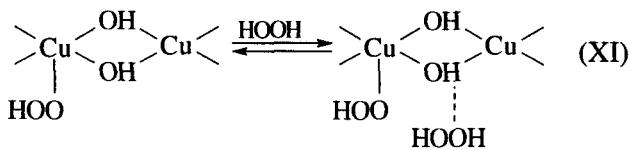
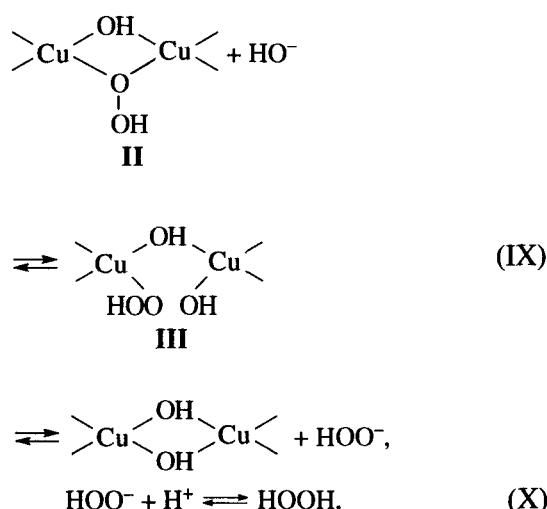


The consequence of these rearrangements is dispersion, that is, an increase in the number of active sites due to the appearance of new terminal copper ions. Also, the transfer of the terminal ligand  $\text{HOO}^-$  into a bridging state and the formation of inactive form **II** becomes difficult. On the other hand, pyridine which is weakly bonded to the metal atom is incapable of radical changes in the composition and structure of the catalyst and its peroxides. Therefore, small pyridine additives do not change the catalytic properties of  $\text{Cu}(\text{OH})_2$  by contrast to bidentate ligands that promote the catalytic activity. It is natural that both ligands, if added in a large excess, are capable of competing with  $\text{H}_2\text{O}_2$  for active coordination sites and inhibit the catalytic process.

**Peroxide decomposition.** The spectra of colloidal  $\text{Cu}(\text{OH})_2$  solutions point to the fact that, upon the completion of  $\text{H}_2\text{O}_2$  decomposition, the catalyst contains at least two forms of peroxy complexes, **I** and **II**, and the latter probably dominates. Slow transformation of the catalyst into its initial state  $\text{Cu}(\text{OH})_2$  occurs via the same reactions (I)–(V). However, because there is no excess  $\text{H}_2\text{O}_2$ , some equilibria are shifted to the different side:



Because peroxide decomposition is faster in an alkali medium than in a neutral medium, we can write down:



In the case of colloidal catalysts,  $\text{O}_2$  is formed in reaction (XII) only up to a certain point, after which the composition of the colloid only slightly changes for many hours, as is evident from the spectra. Supported samples remain in the form of peroxy complexes for weeks, although the concentration of peroxy ligands gradually decreases possibly because of the moisture from air. Both in colloidal and supported samples, copper remains in the  $\text{Cu}(\text{II})$  state, and the hydroxide structure is damaged.

A promoting effect of  $\text{OH}^-$ , bpy, and pyrophosphate on hydroperoxide decomposition can be explained by the transformation of **II** into **III** by reaction (IX) and by the fact that these ligands may substitute the peroxy ligand from the first coordination sphere of copper to increase the concentration of free  $\text{H}_2\text{O}_2$  in the solution and shift reaction (XII) to the right. This is the reason for an increase in the rate and the yield of  $\text{O}_2$  (up to 100%) in the presence of bpy or  $\text{P}_2\text{O}_7^{4-}$ . Unlike the process of  $\text{H}_2\text{O}_2$  decomposition, the kinetic curve of peroxy **II** decomposition (i.e., a decrease in the absorbance at 350 nm) corresponds to the second-order kinetics. Therefore, step (XII) is probably rate-determining in mechanisms (VIII)–(XII).

Thus, when switching from copper aqua ions to polynuclear copper hydroxide, the reaction of  $\text{H}_2\text{O}_2$  decomposition changes the mechanism from radical to molecular, and the latter differs substantially from all known mechanisms. Thus, in the presence of binuclear  $\text{Cu}(\text{II})$  complexes in triethylamine [13] and  $\text{Fe}(\text{III})$  with EDTA in an alkali medium [14], the mechanism of  $\text{H}_2\text{O}_2$  decomposition is also molecular. However, for these catalysts, the reaction pathway involves the consecutive reduction of metal ions in these complexes to form  $\text{Cu}(\text{I})$  and  $\text{Fe}(\text{II})$  by one  $\text{H}_2\text{O}_2$  molecule followed by their reoxidation by another molecule. In the case of hydroxide catalysts, the formation of  $\text{Cu}(\text{I})$  could easily be identified if the reaction occurred via the same mechanism: the reduction of colloidal  $\text{Cu}(\text{OH})_2$  by hydrazine or hydroxylamine leads to the formation of yellow  $\text{Cu}_2\text{O}$  with the maximum of absorbance in 460 nm; as this takes place, the colloidal solution rap-

idly becomes muddy, and the addition of  $H_2O_2$  does not remove precipitation. It is likely that the formation of peroxy complexes as intermediates stabilizes Cu(II) and favors the concerted rather than stepwise mechanism of  $H_2O_2$  decomposition. Moreover, the formation of hydrogen bonds and the layered structure of the hydroxide create favorable conditions for the interaction of the catalyst active center and the reactant in a limited volume by analogy to natural enzymes.

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