## Porphyrin models of natural catalases

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The kinetics of  $H_2O_2$  decomposition in the presence of copper complexes with porphyrins, whose structure is regularly changed, was studied by the volumetric method. The ion-molecular mechanism of the reaction was proposed on the basis of spectrophotometric analysis of the intermediates. The use of these complexes as simple models of natural catalases was shown to be promising.

**Key words:** metal porphyrins, hydrogen peroxide, decomposition reaction, complex catalysis, kinetics, mechanism.

Copper compounds catalyze many reactions and are of great biochemical significance.<sup>1,2</sup> Although the copper-containing enzymes act, as a rule, as oxidases, chelate copper complexes are considered as model catalysts of hydrogen peroxide decomposition (*i.e.*, as models of catalases). The common feature for mechanisms of the particular reactions is the coordination of peroxide species on the metal atom and the existence of two free coordination sites for the copper(II) compound to manifest the catalytic effect.<sup>1</sup>

The well-known ability of metal cations in metal porphyrins to add various ligands (even weak bases) makes it promising to study the mechanism of catalysis of hydrogen peroxide decomposition by metal porphyrins.<sup>3,4</sup> This mechanism remains unsubstantiated in detail. Literature



data show that the important role in one or another mechanism of the process belongs to the coordinated macrocycle along with the metal cation. In the present work, we studied the electronic absorption spectra, kinetics, and mechanism of hydrogen peroxide decomposition in the presence of copper(II) porphyrin complexes (1-4) with the structure of the macrocycle that is changed regularly.

## Experimental

2,3,7,8,12,13,17,18-Octaethylporphine ( $H_2OEP$ ), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine ( $H_2TPP$ ), 2,3,7,8,12,13,17,18-octaethyl-5,10-diphenylporphine ( $H_2DPOEP$ ), and 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20tetraphenylporphine ( $H_2TPOEP$ ) were synthesized and purified according to known procedures.<sup>5,6</sup> The copper(II) complexes were synthesized by the reactions of Cu(AcO)<sub>2</sub> ·  $H_2O$  (analytical grade) with free porphyrins in boiling DMF<sup>7</sup> (DMF (reagent grade) was distilled *in vacuo*). The complexes were extracted from DMF with chloroform or precipitated upon dilution of a cooled reaction mixture with water and purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> in CHCl<sub>3</sub>. The electronic absorption spectra (EAS)<sup>6,8</sup> of the copper(II) porphyrins are presented in Table 1. The individual character of the compounds was confirmed by TLC (see Table 1).

The decomposition of  $H_2O_2$  in the presence of the copper complexes was carried out in a DMF-KOH- $H_2O$  system at 343–363 K and atmospheric pressure in a temperature-controlled reactor with stirring; the volume of the reaction mixture being 10 mL. An aqueous solution of KOH ( $C_{KOH} = 1.77 \cdot 10^{-1}$ mol L<sup>-1</sup>) and an aqueous solution of hydrogen peroxide ( $C_{H_2O_2} =$ (19.9±0.2) mol L<sup>-1</sup>) were added to a solution of the complex

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different catalyst concentrations\*

Complex	Electronic absorption $\lambda_{max}/nm$ (loge	<i>R</i> <sub>f</sub> (hexane : ben-	
	CHCl <sub>3</sub>	DMF*	zene, 1 : 1)
CuOEP	563 (4.54), 528 (4.26), 400 (5.88)	559, 523	0.102
CuTPP	571 (shoulder), 540 (4.26), 416 (5.72)	570, 539	0.586
CuDPOEP	579 (4.08), 544 (4.15), 414 (5.48)	577, 542	0.665
CuTPOEP	566 (4.23), 426 (5.23)	565	0.754

Table 1. Selected parameters of the studied copper(II) porphyrins

\* The region of the Soret band was not studied.

in DMF. The concentrations of the complexes, KOH, and  $H_2O_2$  were varied within  $10^{-6}-10^{-4}$ ,  $(0.18-3.54)\cdot 10^{-2}$ , and 2.98-5.97 mol L<sup>-1</sup>, respectively. The initial concentration of  $H_2O_2$  was determined by iodometric titration.

The decomposition of  $H_2O_2$  without metal porphyrins and in the presence of the copper(II) salts was studied under similar conditions. The decomposition rate was determined volumetrically by measuring the volume of evolved oxygen.

The rates of  $H_2O_2$  decomposition (*W*) were determined from the slope of the linear region of the  $V_{O_2}$  vs.  $\tau$  plot optimized by the least-squares method to the positive direction of the abscissa (Fig. 1). The catalytic activity of the copper complex (*A*) was calculated by dividing *W* into the known concentration of the copper complex (Tables 2–5). The reaction orders (*n*) with respect to  $H_2O_2$  and KOH and the true value of the rate constants *k* were determined by the least-squares optimization of the linear dependences in the logarithmic coordinates of the rate *W* vs. concentration of the corresponding component at constant concentrations of other reactants. The activation energy (*E*) of the reaction was determined from the slope of the



**Fig. 1.** Plots of the volume of evolved O<sub>2</sub> ( $V_{O_2}$ ) vs. time of H<sub>2</sub>O<sub>2</sub> decomposition for CuDPOEP (1), CuTPP (2), and CuOEP (3). Conditions:  $C_{CuDPOEP} = 3.78 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ ,  $C_{CuTPP} = 2.56 \cdot 10^{-6} \text{ mol } \text{L}^{-1}$ ,  $C_{CuOEP} = 8.57 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ ,  $C_{H_2O_2} = 3.98 \text{ mol } \text{L}^{-1}$ ,  $C_{KOH} = 1.77 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ , T = 343 K.

Complex	$C_{\rm CuP} \cdot 10^5$	W	A
	$/mol L^{-1}$	$/mL$ of $O_2 min^{-1}$	$/s^{-1}$
No catalyst		$0.8 \pm 0.2$	
CuOEP	0.122	$1.54{\pm}0.07$	75±3
	1.22	$1.22 \pm 0.06$	$6.0 \pm 0.3$
	3.67	$1.00 {\pm} 0.05$	$1.6 \pm 0.1$
	3.80	$1.50 {\pm} 0.09$	$2.3 \pm 0.1$
	8.57	$1.10 \pm 0.04$	$0.75 {\pm} 0.03$
CuDPOEP	0.27	$0.82 {\pm} 0.02$	$18.0 {\pm} 0.4$
	1.08	$1.57 {\pm} 0.07$	$8.6 {\pm} 0.4$
	3.78	$1.90 {\pm} 0.2$	3.1±0.3
CuTPOEP	0.24	$1.29 \pm 0.09$	32±2
	2.39	$1.40 {\pm} 0.06$	3.48±0.15
	7.16	$1.40 {\pm} 0.1$	$1.2 \pm 0.1$
	16.7	$1.26 {\pm} 0.08$	$0.44 {\pm} 0.03$
CuTPP	0.27	$1.3 \pm 0.1$	30±3
	0.58	$1.48 {\pm} 0.07$	$15.0 {\pm} 0.7$
	1.40	$2.00 {\pm} 0.01$	$7.9{\pm}0.4$
	10.60	$5.40 {\pm} 0.8$	$3.0 {\pm} 0.4$
CuCl <sub>2</sub>	0.98	$0.97 {\pm} 0.08$	$5.9 \pm 0.5$
	1.63	$1.29 \pm 0.12$	$4.7 \pm 0.4$
	8.80	$1.68 {\pm} 0.08$	$1.13 \pm 0.05$
	16.30	$2.00 \pm 0.15$	$0.73 {\pm} 0.06$
$Cu(AcO)_2$	0.58	$1.02 {\pm} 0.08$	$10.5 {\pm} 0.8$
	1.15	$1.2 \pm 0.1$	$6.4 \pm 0.7$
	5.75	$1.5 \pm 0.1$	$1.5 \pm 0.1$
	11.50	1.7±0.2	0.86±0.09

**Table 2.** Rate of  $H_2O_2$  decomposition (*W*) and the catalytic activity (*A*) of the copper(II) porphyrins and copper(II) salts at

\* Conditions: T = 343 K,  $C_{H_2O_2} = 3.98$  mol L<sup>-1</sup>,  $C_{KOH} = 1.77 \cdot 10^{-2}$  mol L<sup>-1</sup>.

straight line in the  $\log W$ -1/*T* coordinates. The activation entropy was calculated by the equation

$$\Delta S^{\neq} = 19.1 \lg W + (E \pm \Delta E) / T - 19.1 \lg T - 205, \tag{1}$$

where  $\Delta E$  is the arithmetic-mean deviation, and T is temperature.

**Table 3.** Rate of  $H_2O_2$  decomposition (*W*) and the catalytic activity of the copper(11) porphyrins (*A*) at different concentrations of KOH\*

Complex	$C_{\rm CuP} \cdot 10^5$	C <sub>KOH</sub>	W	A
	mol I		$/mL \text{ of } O_2 \min^{-1}$	$-1 / s^{-1}$
CuOEP	3.80	0.00177	$0.35 {\pm} 0.01$	$0.54 {\pm} 0.02$
		0.0177	$1.13 \pm 0.09$	$1.76 \pm 0.14$
		0.00181	$1.50 \pm 0.09$	$2.4 \pm 0.1$
		0.0354	$2.20 \pm 0.14$	$3.4 \pm 0.2$
CuTPOEP	2.39	0.00177	$0.39 {\pm} 0.03$	$0.97 {\pm} 0.07$
		0.0177	$1.18 \pm 0.06$	$2.92 \pm 0.15$
		0.0181	$1.42 \pm 0.06$	$3.50 {\pm} 0.15$
		0.0354	$2.0 {\pm} 0.4$	5±1

\* Conditions: T = 343 K,  $C_{H_2O_2} = 3.98$  mol L<sup>-1</sup>.

$C_{\mathrm{H_2O_2}}/\mathrm{mol}\ \mathrm{L^{-1}}$	$W/mL$ of $O_2 min^{-1}$	$A/s^{-1}$
1.72	$0.80 {\pm} 0.04$	1.25±0.06
3.44	$1.50 \pm 0.06$	2.3±0.1
3.98	$1.50 \pm 0.09$	$1.76 \pm 0.14$
5.16	$2.7 \pm 0.2$	$4.2 \pm 0.4$
5.97	$2.9 \pm 0.2$	$4.5 \pm 0.4$

**Table 4.** Rate of  $H_2O_2$  decomposition (*W*) and the catalytic activity of CuOEP (*A*) at different concentrations of  $H_2O_2$ 

\* Conditions: T = 343 K,  $C_{\text{CuOEP}} = 3.8 \cdot 10^{-5} / \text{mol L}^{-1}$ ,  $C_{\text{KOH}} = 1.77 \cdot 10^{-2} \text{ mol L}^{-1}$ .

Electronic absorption spectra of the metal porphyrins were recorded on Specord M-40 and Hitachi U2000 spectrophotometers.

## **Results and Discussion**

The numerical values of the rate of  $H_2O_2$  decomposition are presented in Tables 2–5. The rate W and catalytic activity increase with an increase in the concentrations of KOH and  $H_2O_2$  (see Tables 3 and 4). All catalysts are characterized by satisfactory linear correlations in the logarithmic coordinates between W and the reagent concentration with the slopes of the straight lines (reaction orders with respect to OH<sup>-</sup> and  $H_2O_2$ ) close to 1 (Figs 2 and 3). As can be seen from the data in Table 2, the decomposition of  $H_2O_2$  is catalyzed not at each catalyst concentration. For instance, for CuDPOEP, CuCl<sub>2</sub>, and Cu(AcO)<sub>2</sub>, the catalytic effect of the increase in W over that in the non-catalyzed reaction starts at



**Fig. 2.** Plot of the logarithm of the rate of  $H_2O_2$  decomposition *vs.* KOH concentration in the presence of CuOEP. Conditions:  $C_{\text{CuOEP}} = 3.80 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ ,  $C_{\text{H}_2O_2} = 3.98 \text{ mol } \text{L}^{-1}$ , T = 343 K.

 $C_{\text{CuP}} > 1 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ . For these catalysts, a satisfactory linear correlation is observed in the coordinates of the first-order equation  $W^T = f(C_{\text{catalyst}})^T$  (Fig. 4, curves 2–4). The first order with respect to the CuTPP concentration is also confirmed experimentally (see Fig. 4, curve 1). The reactions catalyzed by the complexes CuOEP and CuTPOEP have the order close to zero with respect to the catalyst concentration (see Table 2).

Thus, for CuDPOEP, CuTPP, CuCl<sub>2</sub>, and Cu(AcO)<sub>2</sub> the kinetic equation has the form

$$dC_{O_2}/d\tau = kC_{H_2O_2}C_{KOH}C_{CuP}(C_{O_2})^0 =$$
  
= kC\_{H\_2O\_2}C\_{KOH}C\_{CuP}, (2)

Complex	$C_{\text{cat}} \cdot 10^5 / \text{mol L}^{-1}$	T/K	$W/mL$ of $O_2 min^{-1}$	$A/{\rm s}^{-1}$	$E/kJ mol^{-1}$	$\Delta S^{\neq}/J \text{ mol}^{-1} \text{ K}^{-1}$
No catalyst		343	$0.8 {\pm} 0.2$		72±4	-45±12
		353	$1.7 \pm 0.2$			
		363	$3.2 \pm 0.3$			
CuCl <sub>2</sub>	8.80	343	$1.68 {\pm} 0.08$	$1.13 \pm 0.05$	52±7	$-86\pm23$
		353	$2.2 \pm 0.2$	$1.5 \pm 0.1$		
		363	$4.7 \pm 0.4$	$3.0 \pm 0.3$		
CuOEP	3.80	343	$1.5 \pm 0.06$	$2.3 \pm 0.09$	39±3	$-136\pm10$
		353	$2.10 \pm 0.06$	$3.18 {\pm} 0.09$		
		363	$3.2 \pm 0.4$	$4.6 \pm 0.5$		
CuDPOEP	1.08	343	$1.57 {\pm} 0.07$	$8.6 {\pm} 0.4$	17±2	$-200\pm 6$
		353	$1.95 \pm 0.03$	$10.4 \pm 0.15$		
		363	$2.21 \pm 0.04$	$11.5 \pm 0.2$		
CuTPOEP	2.39	343	$1.40 {\pm} 0.06$	$3.48 {\pm} 0.15$	39±5	$-137\pm17$
		353	$1.85 \pm 0.06$	$4.45 \pm 0.1$		
		363	$3.0 \pm 0.3$	$6.9 \pm 0.6$		
CuTPP	1.40	343	$2.00 {\pm} 0.01$	$7.90 {\pm} 0.04$	27±3	$-169 \pm 10$
		353	$2.5 \pm 0.2$	$10.6 \pm 0.9$		
		363	$3.4{\pm}0.4$	14±2		

**Table 5.** Rate of  $H_2O_2$  decomposition (W) and the catalytic activity of the copper(11) porphyrins (A) at different temperatures

\* Conditions:  $C_{\text{H}_2\text{O}_2} = 3.98 \text{ mol } \text{L}^{-1}$ ,  $C_{\text{KOH}} = 1.77 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ .



**Fig. 3.** Plot of the logarithm of the rate of  $H_2O_2$  decomposition *vs.* logarithm of  $H_2O_2$  concentration in the presence of CuOEP. Conditions:  $C_{\text{CuOEP}} = 3.80 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ ,  $C_{\text{KOH}} = 1.77 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ , T = 343 K.

and for CuOEP and CuTPOEP,

$$dC_{O_2}/d\tau = k'C_{H_2O_2}C_{KOH}(C_{CuP})^0(C_{O_2})^0 =$$
  
= k'C\_{H\_2O\_2}C\_{KOH}. (3)

Taking into account the obtained expressions for the rates of processes (2) and (3), we can assume that heterogeneous catalysis occurs in the case of CuOEP and CuTPOEP. In fact, precipitates appeared at some concentrations of the complexes. It is these complexes that have the lowest solubility in organic solvents among the complexes studied in the present work. To confirm this assumption, freshly prepared mixtures of solutions of the copper complexes in DMF with hydrogen peroxide and with KOH were studied. No apparent changes first occur in the EAS upon addition of alkali. In the case of CuOEP and CuTPOEP, the addition of  $H_2O_2$  violates the Lambert—Bouger—Beer law, and then the solutions be-



**Fig. 4.** Plots of the rate of  $H_2O_2$  decomposition vs. concentration of CuTPP (1), CuDPOEP (2), CuCl<sub>2</sub> (3), and Cu(AcO)<sub>2</sub> (4). Conditions:  $C_{H_2O_2} = 3.98 \text{ mol } \text{L}^{-1}$ ,  $C_{\text{KOH}} = 1.77 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ , T = 343 K.

come noticeably turbid. The spectrum of the liquid phase exhibits a bathochromic shift (by 9–13 nm) of band I, as is the case immediately after the addition of a KOH–H<sub>2</sub>O<sub>2</sub> mixture. Sharp decrease in the relative intensity of the long-wavelength absorption occurs simultaneously and the absorption background at 450–500 nm increases. The EAS of the initial and final (after settling of the solutions) reaction products of CuOEP and CuTPOEP with H<sub>2</sub>O<sub>2</sub> in the presence of KOH are shown in Fig. 5. As is known,<sup>9</sup> such EAS are characteristic of the  $\pi$ -radical cation forms of metal porphyrins.

Changes in the absorption spectra are observed in the homogeneous reaction mixtures (CuTPP and CuDPOEP



**Fig. 5.** Electronic absorption spectra of CuOEP (1), CuTPOEP (2), and CuDPOEP (3) in DMF and of CuOEP (4), CuTPOEP (5), and CuDPOEP (6) in DMF-KOH-H<sub>2</sub>O<sub>2</sub>. Conditions: T = 298 K,  $\tau = 1800$  s,  $C_{KOH} = 1.77 \cdot 10^{-2}$  mol L<sup>-1</sup>,  $C_{H_2O_2} = 3.98$  mol L<sup>-1</sup>.

catalysts). The electronic absorption spectra of the complexes in DMF remain virtually unchanged upon the addition of KOH or H<sub>2</sub>O<sub>2</sub>. Sharp changes in the spectra of these complexes recorded before gas evolution are observed only when KOH and H<sub>2</sub>O<sub>2</sub> are added simultaneously. For the CuDPOEP-catalyzed reaction, the spectrum changes similarly to those described above for the heterogeneous systems (see Fig. 5, curves 5 and 6). The EAS of the reaction mixture containing CuTPP cannot be recorded because of vigorous oxygen evolution. However, after CuTPP was removed from the reaction mixture by extraction with chloroform, the EAS exhibit the absorption of the initial CuTPP ( $\lambda^{I}_{max} = 538.5$  nm) and its  $\pi$ -radical cation form ( $\lambda^{I}_{max} = 700$  nm and  $\lambda^{II}_{max} =$ 664 nm). It can be seen from the spectral data that CuTPP and CuDPOEP do not react with  $H_2O_2$  in the absence of KOH, unlike CuOEP and CuTPOEP and similar manganese(III) complexes studied earlier.<sup>10</sup> As will be shown below, this difference in reactivity can be explained by variable stability of the axial CuP complexes with an  $H_2O_2$  molecule.

For the systems studied, the kinetics of the process can be interpreted taking into account elementary reactions of coordination of  $H_2O_2$  on the central atom of the catalyst molecule and then its decomposition with twoelectron oxidation ((4), (5)), equilibrium of acidic dissociation of hydrogen peroxide under the action of alkali (6), and catalyst reduction to the initial state by the reaction with  $HO_2^-$  (7)

$$CuP + H_2O_2 \xrightarrow{k_1} (H_2O_2)CuP, \qquad (4)$$

$$(H_2O_2)CuP \xrightarrow{k_2} (O^{2-})CuP^{++} + H_2O,$$
 (5)

$$H_2O_2 + OH^- \xrightarrow{k_3, K} HO_2^- + H_2O,$$
 (6)

$$(O^{2-})CuP^{++} + HO_2^{-} \xrightarrow{k_4} CuP + OH^{-} + O_2.$$
 (7)

i. Fast, ii. slow.

A kinetic equation (8) for the rate-determining step (7) can be written in the form

$$-dC_{\text{HO}_{2}^{-}}/d\tau = dC_{\text{O}_{2}}/d\tau = k_{4}C_{(\text{O}_{2}^{-})\text{CuP}^{+}} \cdot C_{\text{HO}_{2}^{-}} =$$
$$= k_{4}KC_{\text{CuP}}C_{\text{H}_{2}\text{O}_{2}}C_{\text{OH}^{-}}.$$
(8)

In the case of the heterogeneous reaction, the term  $C_{(O_2^-)CuP^+}$ . does not enter into kinetic equation (8). A comparison of Eqs (2) and (8) and the data in Table 5 show that the proposed scheme of reactions (4)—(7) agrees well with the experimental kinetic equation (2) of H<sub>2</sub>O<sub>2</sub> decomposition and the activation parameters; in this case, the rate  $W = k_4 K$ . The negative activation entropy for the

catalytic reactions confirms the nature of rate-determining step (7) with the transition state in which the reactant  $HO_2^-$  is axially coordinated on the catalyst.

Thus, the catalytic activity of the studied metal porphyrins in the decomposition of  $H_2O_2$  is due to the ability of the copper atom in the complex to additionally coordinate the ligands (coordination number 5), as in functioning of the natural catalase<sup>1</sup>, and low ionization potentials of the coordinated porphyrin macrocycle. As supposed above, based on the spectrophotometric data, the inertness of CuTPP and CuDPOEP in the reaction with  $H_2O_2$ (in the absence of KOH) is actually related to their low ability to axial coordination. Weak retention of the  $O^{2-}$ ligand in the  $(O^{2-})CuP^+$   $\pi$ -radical complex eliminated during reduction in the slow step (8) decreases the activation energy in the case of the complexes CuTPP and CuDPOEP (see Table 5) compared to other metal porphyrins.

Among the studied metal porphyrins, CuTPP and CuDPOEP exhibit substantial catalytic activity in  $H_2O_2$ decomposition (see Table 2). They increase the reaction rates and decrease the activation energy 3-4-fold compared to that in the noncatalytic process. The activity of the complexes CuOEP and CuTPOEP is comparable with that of the copper salts. Under experimental conditions (see Tables 2–5), the conversion of  $H_2O_2$  is low. After the end of the reaction (after the time interval for which the kinetic curve remains linear),  $\sim 90\%$  of H<sub>2</sub>O<sub>2</sub> remain in the system, which is confirmed by iodometric titration. The study of the influence of addition of copper porphyrin to the mixture after the end of the reaction (in the region of kinetic curve saturation) for the heterogeneous process showed the absence of a change in the rate of  $H_2O_2$  decomposition. Similarly addition of  $H_2O_2$  to the reaction mixture resumes gas evolution with a rate somewhat lower than the initial rate of the process. This indicates that the catalyst undergoes no destruction during the catalytic process, unlike the catalyst (Cl)MnTPP.<sup>10</sup> In the latter case, the reaction proceeds under homogeneous conditions, which allows one to compare the results for CuTPP and (Cl)MnTPP. The reaction of peroxide decomposition catalyzed by the copper complex occurs twice as fast. Under the same conditions of the reaction  $(T = 298 \text{ K}, C_{\text{MP}} = (10.6-11.6) \cdot 10^{-5}, C_{\text{KOH}} = (1.8-1.9) \cdot 10^{-2}$ , and  $C_{\text{H}_2\text{O}_2} = 3.98 \text{ mol } \text{L}^{-1}$ ), the value of *W* and the activation energy *E* for the Cu and Mn complexes are equal to  $(5.4\pm0.8)$ ,  $(2.6\pm0.1)$  mL of O<sub>2</sub> min<sup>-1</sup> and  $(25\pm3)$ ,  $(47\pm1)$  kJ mol<sup>-1</sup>, respectively. The enhanced catalytic activity of CuTPP compared to that of (Cl)MnTPP is probably due to the absence of steric hindrance for coordination of an H<sub>2</sub>O<sub>2</sub> molecule at both sides of the macrocycle plane.

Thus, the results of studies on EAS and kinetics of the reactions in the CuP-KOH- $H_2O_2$  system indicate the ion-molecular mechanism of  $H_2O_2$  decomposition cata-

lyzed by the copper(II) porphyrins, which makes it possible to consider the latter as simple models of catalases and oxidoreductases. The gradual transition from the octaalkyl-substituted copper complex to the tetraphenylporphyrin complex in the series CuOEP, CuDPOEP, CuTPOEP, and CuTPP is accompanied by the regular smooth change in the catalytic properties of the complexes because of their different solubility and phase conditions of the catalytic process. However, functional substitution should be considered as a method for controlling the catalytic activity of the metal porphyrins. Investigations similar to those considered in the present work should be continued for a wider set of the porphyrin catalysts to establish correlations between the catalytic activity and constants of substituents.

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