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# Kinetics and Mechanism of the Reaction of Manganese(III) Octaethylporphine with Hydrogen Peroxide

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**Abstract** — A spectroscopic and kinetic study of the oxidation of (chloro)(octaethylporphinato)manganese(III) (Cl)MnOEP with hydrogen peroxide in an aqueous–organic medium at 288–308 K was made. The nature and composition of the reaction products differ depending on the reaction conditions ($H_2O_2$ concentration). Based on the data on reaction rates, thermodynamic parameters of activation, and form of the rate equations of the (Cl)MnOEP oxidation, a multistep reaction mechanism is suggested and substantiated, in which the decisive role is played by the limiting step, two-electron oxidation of the metal porphyrin with the coordinated peroxide or partial reduction of the oxidized form of the manganese porphyrin with the second peroxide molecule (in the form of $HO_2^-$), and by acid–base equilibria of the peroxide.
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After elucidating the potential of manganese complexes as redox catalysts and understanding their role in medicine, agriculture, and other fields, the interest in these compounds steadily grows. Consideration of the role of manganese in photosystem **II** of the photosynthesis, in enzymatic processes, and also in model systems simulating the functional properties of various enzymes [1] demonstrated the significance of manganese compounds in vital functions. Of particular importance are manganese complexes with porphyrins, because in their presence many reactions occur under milder conditions and in media in which simpler manganese derivatives are inert or nonspecific [1]. By using manganese complexes with various porphine derivatives and various coordination centers and by varying the solvents and temperature, it is possible to ensure selective decomposition of hydrogen peroxide, thus simulating the effect of catalases.

The most significant results in this field were obtained in [2–7]. A study of the kinetics of $H_2O_2$ decomposition in the presence of manganese(III) tetra(2,6-dimethyl-3-sulfonatophenyl)porphine at pH 7.6–12.1 led to a conclusion that the reaction involves equilibrium coordination of a hydrogen peroxide molecule with the catalyst, followed by slow formation of the π radical cation form of oxomanganese(IV) porphyrin or oxomanganese(V) porphyrin [2].

Formation of the oxo complexes $(O)Mn^{IV}P$, $[(O)Mn^{IV}P]^{+\cdot}$, and $(O)Mn^{V}P$ (P is the porphyrin dianion), readily transforming into each other, is also noted in experiments on the use of manganese porphyrin–peroxide systems for oxidation and epoxidation of aliphatic, unsaturated, and aromatic compounds [3–7]. For example, the reaction of peracetic acid with manganese(III) tetra(2,6-dichloro-4-R-phenyl)porphyrin (RTDCPP, R = $CH_3O$, H, Br, Cl, $NO_2$) complexes in an acetonitrile–acetic acid mixture leads to the formation of an intermediate catalyst–oxidant complex [5]. In the course of catalytic oxidation of *cis*-stilbene and naphthalene, the intermediate complex [(HOAc)·MnRTDCPP](X) formed by replacement of the anion (X) with an HOAc molecule in the inner coordination sphere irreversibly transforms into a mixture of two high-valence oxomanganese complexes. It is assumed that the complexes have the compositions (X)(O)·$Mn^{V}$RTDCPP and $[(O)Mn^{IV}RTDCPP]^{+\cdot}(X)$ [6]. The first complex is responsible for the epoxidation of cis-stilbene, and the second complex, for the hydroxylation of naphthalene. In $CH_3CN$, the formation of the stable complex is manifested as appearance of absorption at 415 nm in the course of the reaction of (Cl)MnTDCPP with peracetic acid, whereas in $CH_2Cl_2$ this complex is short-lived and readily decomposes with the breakdown of the macroring [7].

The transformations of the catalysts were judged in these papers mainly from the transformations of the reactants or special compounds-traps, as in [2], whereas the state of the catalyst itself (metal porphy-

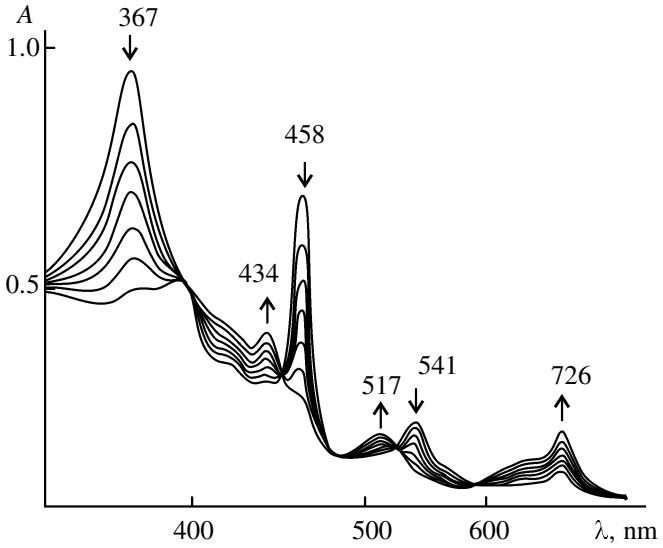



**Fig. 1.** Evolution of the electronic absorption spectrum of (Cl)MnOEP in the course of the reaction with $H_2O_2$ (298 K, $C_{H_2O_2}$ = 1.0 M). (*A*) Optical density. Arrows denote the direction of the spectrum evolution.

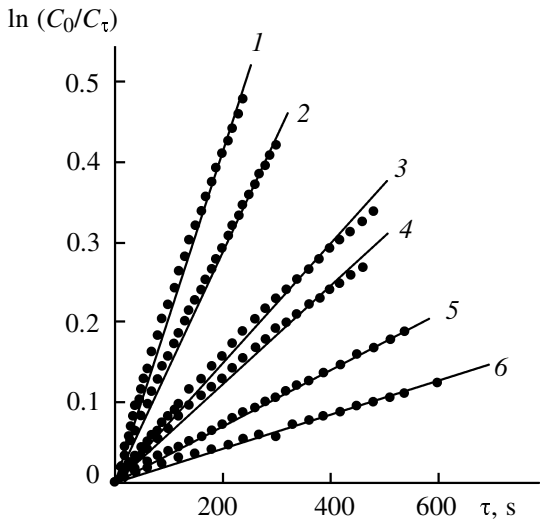



**Fig. 2.** $\ln(C_0/C_\tau)$–τ plot for the reaction of (Cl)MnOEP with $H_2O_2$. $C_{(Cl)Mn^{III}OEP} = 2 \times 10^{-5}$ M. $C_{H_2O_2}$, M: (*1*) 0.33, (*2*) 0.49, (*3*) 0.05, (*4*) 1.35, (*5*) 0.03, and (*6*) 0.01. *T*, K: (*1*) 308, (*2*) 303, (*3*) 298, and (*4*–*6*) 293. $R^2$ = 0.99.

rin) was not examined. Therefore, this study deals with the direct reaction of manganese porphyrins with the oxidant, $H_2O_2$. Previously, using the spectrophotometric method, we studied the kinetics of the reactions of mixed acido tetraphenylporphinato manganese(III) complexes [(X)MnTPP] with hydrogen peroxide in DMF [8, 9]. We found that the decisive role in the coordination of $H_2O_2$ with the porphyrin complex is played by the coordination unsaturation of the Mn atom, which is mainly controlled by the state of bonds with the coordinated macroring. The structure of the macroring and degree of its aromaticity can be considered as the means to control the oxidation process. Studies of the structure–reactivity relationship for porphyrin–hydrogen peroxide systems are yet in the initial stage of the development.

Here we report the results of a spectrophotometric and kinetic study of the reaction of (chloro)(octaethylporphinato)manganese(III) (Cl)MnOEP with hydrogen peroxide in water–DMF at 288–308 K.

The electronic absorption and IR spectra correspond to a five-coordinate compound of the composition (Cl)MnOEP (see Experimental, [10]).

The reaction of (Cl)MnOEP with $H_2O_2$ at temperatures close to room temperature is accompanied by changes in the electronic absorption spectra, with isobestic points at 394, 446, 478, 523, and 582 nm (Fig. 1). This pattern suggests mutual transformation of two stable colored compounds, one of which is the starting (Cl)MnOEP whose speciation differs depending on the hydrogen peroxide concentration (see below). The intensity of the absorption bands of the starting (Cl)MnOEP at 367, 458, and 541 nm decreases, and that of the bands at 434, 517, and 726 nm increases. The final product was identified using published data [11–13]. The spectrum of the final product corresponds to the π radical cation of manganese(III) octaethylporphine (Fig. 1). The pattern shown in Fig. 1 is typical for the whole examined range of $H_2O_2$ concentrations, which distinguishes the octaethylporphine complex from (Cl)MnTPP studied in [8, 9], for which the analogous reaction gave different products depending on $C_{H_2O_2}$. The reaction of (Cl)·MnOEP with $H_2O_2$ is first-order with respect to the metal porphyrin, as demonstrated by data in Fig. 2. The apparent rate constants of the reaction are given in Table 1.

The reaction order with respect to $[H_2O_2]$ is variable. The examined interval of $H_2O_2$ concentrations can be subdivided into three ranges: 0.01–0.07, 0.2–0.52, and 1.00–2.22 M, with specific order with respect to hydrogen peroxide (*n*) in each range (Figs. 3, 4): 1/2, 0, and –1/2, respectively, as judged from the slope of the straight lines in the coordinates $\log k_{app}^T$–($-\log C_{H_2O_2}$). The zero reaction order follows from the lack of the dependence of $k_{app}$ on $C_{H_2O_2}$ (Table 1).

The results obtained allow us to write the following experimental overall rate equations for the first, sec-

**Table 1.** Apparent kinetic parameters of the reaction of (Cl)MnOEP with $H_2O_2$ in DMF

| $C_{H_2O_2}$, M | $k_{app} \times 10^4$, $s^{-1}$ | | | | $E'$, kJ $mol^{-1}$ | $\Delta S^{\neq}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|---|
| | 293 K | 298 K | 303 K | 308 K | | |
| 0.01 | 2.9±0.2 | 4.6±0.1 | 7.2±0.3 | 11.0±0.4 | 67±1 | –91±3 |
| 0.03 | 5.0±0.1 | 8.1±0.3 | 12.3±0.2 | 17.8±0.3 | 63±2 | –100±7 |
| 0.05 | 6.1±0.2 | 10.0±0.4 | 14.6±0.5 | 22.9±0.4 | 65±2 | –91±7 |
| 0.07 | 8.6±0.5 | 12.2±0.4 | 18.8±0.8 | 25.7±1.0 | 56±2 | –120±7 |
| 0.20 | 10.2±0.4 | 16.4±0.7 | 25.0±1.0 | 32.6±0.9 | 59±4 | –107±13 |
| 0.33 | 10.3±0.6 | 16.4±0.6 | 24.0±1.3 | 31.3±0.8 | 56±4 | –118±13 |
| 0.49 | 9.8±0.5 | 15.8±0.4 | 20.7±0.6 | 31.7±0.6 | 57±4 | –115±13 |
| 0.52 | 10.0±0.7 | 15.9±0.8 | 22.5±1.1 | 30.3±1.0 | 55±3 | –121±10 |
| 1.00 | 9.5±0.2 | 13.1±0.5 | 17.8±0.5 | 25.8±0.5 | 50±2 | –140±7 |
| 1.35 | 8.5±0.3 | 10.9±0.3 | 16.3±0.6 | 22.3±0.5 | 49±3 | –144±10 |
| 1.72 | 7.3±0.2 | 9.9±0.2 | 14.9±0.5 | 19.7±0.6 | 51±2 | –138±7 |
| 2.22 | 6.1±0.3 | 8.1±0.2 | 11.4±0.5 | 16.6±0.5 | 50±2 | –143±7 |

ond, and third ranges of $H_2O_2$ concentrations, respectively:

$$-dC_{(Cl)Mn^{III}OEP}/d\tau = k_{v1}C_{(Cl)Mn^{III}OEP}C^{1/2}_{H_2O_2}, \quad (1)$$

$$-dC_{(Cl)Mn^{III}OEP}/d\tau = k_{v2}C_{(Cl)Mn^{III}OEP}, \quad (2)$$

$$-dC_{(Cl)Mn^{III}OEP}/d\tau = k_{v3}C_{(Cl)Mn^{III}OEP}C^{-1/2}_{H_2O_2}. \quad (3)$$

The true rate constants $k_{v1}$ and $k_{v3}$ found by optimization of the dependences shown in Figs. 3 and 4, and also the activation parameters of the reaction are listed in Table 2.

Taking into accouint the spectral data (Fig. 1) and Eq. (3), we can suggest for the first range of $H_2O_2$ concentrations the following scheme of elementary steps, consistent with Eq. (1):

$$H_2O_2 \overset{K_1}{\rightleftarrows} H^+ + HO_2^-. \quad (4)$$

$$(Cl)Mn^{III}OEP + HO_2^- \overset{K_2}{\rightleftarrows} (Cl)(HO_2^-)Mn^{III}OEP, \quad (5)$$

$$(Cl)(HO_2^-)Mn^{III}OEP \xrightarrow[slow]{k_3} O{=}Mn^{III}(OEP^{+\cdot}) + OH^- + Cl^-. \quad (6)$$

The perhydroxide anion present in the system in equilibrium concentrations in accordance with Eq. (4) reversibly adds [reaction (5)] to the coordination-unsaturated Mn atom, forming the donor–acceptor bonds $-O^-\rightarrow Mn$. Hydrogen peroxide is coordinated by manganese(III) octaethylporphine not in the form of the $H_2O_2$ molecule, as in the case of the complexes (X)MnTPP considered in [8, 9], but in the form of a stronger nucleophile, $HO_2^-$, apparently because of a

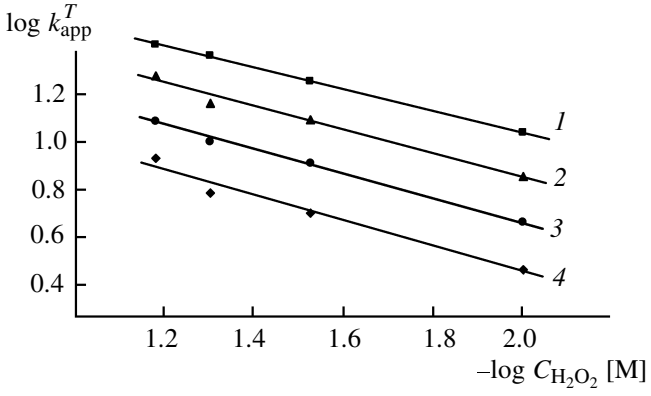



**Fig. 3.** Plot of $\log k^T_{app}$ vs. $-\log C_{H_2O_2}$ for the reaction of (Cl)MnOEP with $H_2O_2$ in the $H_2O_2$ concentration range 0.01–0.07 M. *T*, K: (*1*) 308, (*2*) 303, (*3*) 298, and (*4*) 293; $R^2$ = 0.98.

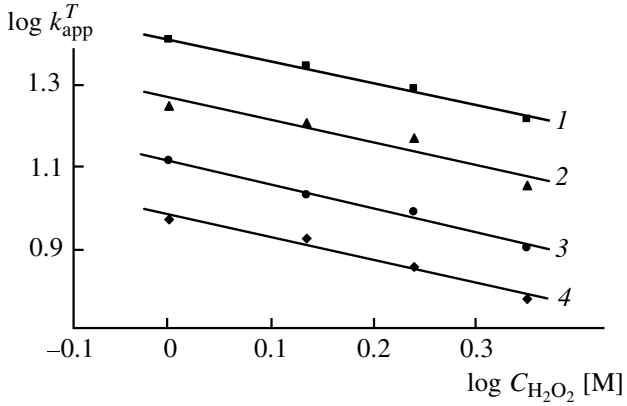



**Fig. 4.** Plot of $\log k^T_{app}$ vs. $\log C_{H_2O_2}$ for the reaction of (Cl)MnOEP with $H_2O_2$ in the $H_2O_2$ concentration range 1.00–2.22 M. *T*, K: (*1*) 308, (*2*) 303, (*3*) 298, and (*4*) 293; $R^2$: (*1, 3, 4*) 0.98 and (*2*) 0.92.

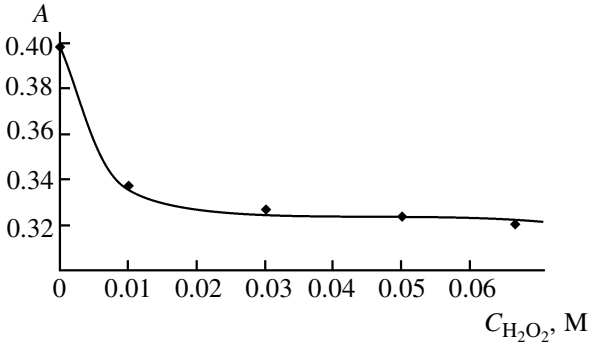



**Fig. 5.** Titration curve of the complex (Cl)$Mn^{III}$OEP with hydrogen peroxide in DMF.

decrease in the effective positive charge $\delta^+$ on the Mn atom in going from the tetraphenylporphine to octaethylporphine complex as a result of electron-donor effect of eight β-alkyl substituents and elimination of the electron-withdrawing effect of the *meso*-phenyl groups. The perhydroxide ion activated by the coordination with Mn transfers the oxygen atom to the metal porphyrin, with the elimination of $OH^-$ in the slow two-electron redox reaction (6). (Cl)MnOEP transforms into the oxidized species, O=$Mn^{III}$($OEP^{+\cdot}$), which is readily identified by the electronic absorption spectrum (Fig. 1). Because of the low concentration of $HO_2^-$, the oxidized form of the complex does not interact with the second peroxide molecule, in contrast to all the catalytic processes of $H_2O_2$ disproportionation.

Apparently, $HO_2^-$ coordinates [reaction (5)] at the sixth coordination site, with the $Cl^-$ ligand remaining in the coordination sphere. This was confirmed by the example of (X)MnTPP [8] for which a strong dependence of the reaction rate on the nature of (X) was revealed.

**Table 2.** True rate constants and activation energies and entropies for the reaction of (Cl)MnOEP with $H_2O_2$ in DMF

| $C_{H_2O_2}$ range, M | $T$, K | $k_v \times 10^3$, $s^{-1}\,mol^{-1}\,l$ | $E$, kJ $mol^{-1}$ | $\Delta S^{\neq}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|
| 0.01–0.07 | 293 | 3.0 ± 0.1 | 63 ± 1 | –85 ± 3 |
| | 298 | 4.6 ± 0.1 | | |
| | 303 | 7.2 ± 0.1 | | |
| | 308 | 10.4 ± 0.4 | | |
| 1.00–2.22 | 293 | 0.95 ± 0.02 | 50 ± 2 | –140 ± 6 |
| | 298 | 1.27 ± 0.02 | | |
| | 303 | 1.8 ± 0.1 | | |
| | 308 | 2.55 ± 0.02 | | |

The rate equation for the limiting step is as follows:

$$-dC_{(Cl)(HO_2^-)Mn^{III}OEP}/d\tau = k_3 C_{(Cl)(HO_2^-)Mn^{III}OEP}. \quad (7)$$

After expressing $C_{(Cl)(HO_2^-)Mn^{III}OEP}$ through the equilibrium constant $K_2$ and then $C_{HO_2^-}$ through the equilibrium constant $K_1$, we obtain Eq. (8):

$$-dC_{(Cl)(HO_2^-)Mn^{III}OEP}/d\tau = -dC_{(Cl)Mn^{III}OEP}/d\tau = k_3 K_2 C_{(Cl)Mn^{III}OEP} C^{1/2}_{H_2O_2} K_1^{1/2}. \quad (8)$$

The first equality in Eq. (8) was written taking into account equilibrium (5). Thus, from comparison of Eqs. (1) and (8) we obtain Eq. (9):

$$k_{v1} = k_3 K_1^{1/2} K_2, \quad (9)$$

where $K_1 = 2.4 \times 10^{-12}$ at 298 K [14].

To determine the numerical value of $K_2$, we performed spectrophotometric titration of a (Cl)$Mn^{III}$OEP solution in DMF with hydrogen peroxide (Fig. 5). The titration curve has a single step. From the slope (with respect to abscissa) of the straight line in the coordinates logarithm of the ratio of the equilibrium concentration of (Cl)$(HO_2^-)Mn^{III}$OEP to that of (Cl)·$Mn^{III}$OEP (indicator ratio) vs. logarithm of $C_{H_2O_2}$, we determined the number of the added $H_2O_2$ molecules: 1/2. The concentration equilibrium constant of the coordination of the peroxide in the molecular form, which can be assumed equal to the thermodynamic constant taking into account high dilution, is $(2.2 \pm 0.3) \times 10^{-5}$ $mol^{-1/2}\,l^{1/2}$ at 298 K. Hence, the equilibrium constant of reaction (5) is $K_2 = (9 \pm 1) \times 10^6$ $mol^{-3/2}\,l^{3/2}$, provided that the above value of $K_1$ is given in the molar scale, which does not explicitly follow from the results of [14]. The rate constant of elementary reaction (6) at 298 K is $k_3 = k_{v1}/(K_1^{1/2}K_2) = (3.3 \pm 0.3) \times 10^{-4}$ $s^{-1}$. Note that the dimension of $k_3$ corresponds to Eqs. (6) and (7), which confirms the above assumption concerning the dimension of $K_1$.

For the third range of $H_2O_2$ concentrations, described by rate equation (3), the following five reactions should be taken into account:

$$H_2O_2 \overset{K_1}{\rightleftarrows} H^+ + HO_2^-, \quad (10)$$

$$(Cl)Mn^{III}OEP + HO_2^- \xrightarrow[fast]{k_2} (Cl)(HO_2^-)Mn^{III}OEP, \quad (11)$$

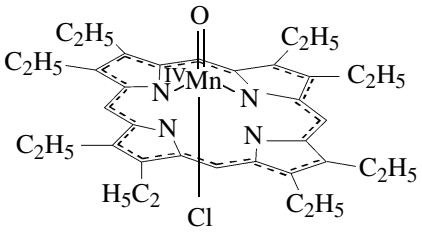
$$(Cl)(HO_2^-)Mn^{III}OEP \overset{K_3}{\rightleftarrows} (Cl)O{=}Mn^{IV}(OEP^{+\cdot}) + OH^-, \quad (12)$$

$$OH^- + H_2O_2 \overset{K_4}{\rightleftarrows} HO_2^- + H_2O, \quad (13)$$

$$2(Cl)O{=}Mn^{III}(OEP^{+\cdot}) + HO_2^- \xrightarrow[\text{slow}]{k_5} 2O{=}Mn^{III}(OEP^{+\cdot}) + HCl + O_2 + Cl^-. \quad (14)$$

Because of the low $HO_2^-$ concentration, no gas evolution is observed in the experiment, and the released $O_2$, apparently, remains in the solution.

The first step involving manganese porphyrin (11), coordination of hydrogen peroxide in the form of $HO_2^-$ at the sixth coordination site of the Mn atoms, at higher $H_2O_2$ concentrations is fast and irreversible. The transfer of two electrons from the readily polarizable porphyrin macroring and metal cation to the coordinated peroxide molecule occurs in equilibrium step (12). Probably, this step is equilibrium because of decreased, compared to $O{=}Mn^{III}(OEP^{+\cdot})$ [Eq. (6)], stability of the π radical cation $(Cl)O{=}Mn^{IV}(OEP^{+\cdot})$ and the higher concentrations of the negative ions $HO_2^-$ and $OH^-$ preventing the ionization of the $Cl^-$ ligand. The latter remains in the coordination sphere of the π radical cation (see scheme below). Finally, the reaction with the second $H_2O_2$ molecule (in the form of $HO_2^-$) becomes possible; this reaction is slower than reaction (11) and limits the process. The reduction of the π radical cation of manganese(IV) porphyrin does not go to completion (i.e., to formation of relatively stable $O{=}Mn^{IV}OEP$) but stops at the step of the one-electron-reduced form $O{=}Mn^{III}(OEP^{+\cdot})$ which is detected in the experiment as a relatively stable final product. This is one more distinction of the system in hand from the system $(Cl)Mn^{III}TPP$–$H_2O_2$ [6] in which the final product is the two-electron-reduced form.




In the course of extraction into chloroform after the reaction of (Cl)MnOEP with $H_2O_2$ and washing to remove excess $H_2O_2$, the radical cation form $O{=}Mn^{III}(OEP)^{+\cdot}$ does transform into the $Mn^{IV}$ complex. The bands appearing in the electronic absorption spectrum at 394, 450 sh, 514, 546, and 667 nm are indicative of the formation of $O{=}Mn^{IV}OEP$. This compound, in turn, slowly (over a period of a day) transforms in solution into manganese(III) porphyrin showing characteristic absorption at about 473 nm (well-known fact in the chemistry of manganese porphyrins [11]).

The rate equation for the limiting step has the form

$$-dC_{(Cl)O{=}Mn^{IV}(OEP^{+\cdot})}/d\tau = k_5 C_{(Cl)O{=}Mn^{IV}(OEP^{+\cdot})} C_{HO_2^-}. \quad (15)$$

From the expression for $C_{(Cl)O{=}Mn^{IV}(OEP^{+\cdot})}$, via the equilibrium constants $K_3$ [Eq. (16)] and $K_4$ [Eq. (17)], we obtain Eq. (18):

$$C_{(Cl)O{=}Mn^{IV}(OEP^{+\cdot})} = K_3 C_{(Cl)(HO_2^-)Mn^{III}OEP} C_{OH^-}^{-1}, \quad (16)$$

$$C_{OH^-} = C_{HO_2^-}^2 K_4^{-1}, \quad (17)$$

$$C_{(Cl)O{=}Mn^{IV}(OEP^{+\cdot})} = K_3 C_{(Cl)(HO_2^-)Mn^{III}OEP} K_4 C_{HO_2^-}^{-2}. \quad (18)$$

Taking into account (10), we express $C_{HO_2^-}$ as follows:

$$C_{HO_2^-} = K_1^{1/2} C_{H_2O_2}^{1/2}. \quad (19)$$

After substituting in Eq. (15) expressions (18) and (19) for the concentrations, we obtain Eq. (20) consistent with the experimental Eq. (3):

$$-dC_{(Cl)O{=}Mn^{IV}(OEP^{+\cdot})}/d\tau = -dC_{(Cl)Mn^{III}OEP}/d\tau = k_5 K_3 K_4 C_{(Cl)(HO_2^-)Mn^{III}OEP} C_{HO_2^-}^{-1} = k_5 K_3 K_4 K_1^{1/2} C_{(Cl)Mn^{III}OEP} C_{H_2O_2}^{-1/2}. \quad (20)$$

Thus, we obtain expression (21),

$$k_{v3} = k_5 K_3 K_4 K_1^{1/2}, \quad (21)$$

in which $K_1 = 2.4 \times 10^{-12}$ at 298 K.

Somewhat different mechanism of the reaction of the octaethylporphine complex with $H_2O_2$, compared to complexes with $H_2TPP$, is caused by difference in the electronic states of the aromatic ligand. This can be confirmed by comparison of the quantitative characteristics of the reactions. The complex (Cl)MnTPP reacts with $H_2O_2$ considerably faster [8] than does (Cl)MnOEP. The true reaction constant is by an order of magnitude higher in the case of (Cl)MnTPP at both low and high $H_2O_2$ concentrations, and the reaction of (Cl)MnTPP with $H_2O_2$ is characterized by more negative $\Delta S^{\neq}$ values.

In the case of (Cl)MnTPP, the π radical cation species is formed only at low $H_2O_2$ concentrations, and at $C_{H_2O_2} > 0.1$ M the final reaction product is the complex with oxidized Mn, manganese(IV) tetraphenylporphine. In the case of (Cl)MnOEP, the final reaction product in the entire range of $H_2O_2$ concentrations is the π radical cation of manganese(III) octaethylporphine. Hence, by varying the electronic state of the macroring and Mn–N bonds, it is possible to attain optimal parameters of the coordination of the

$H_2O_2$ molecules and $HO_2^-$ ions in different steps of the reaction with peroxide and then to use these results for the development of synthetic catalases.

## EXPERIMENTAL

The complex (Cl)MnOEP was prepared and purified by Adler's procedure [15]. For this purpose, 0.03–0.05 g of octaethylporphine purified chromatographically was dissolved in 15–20 ml of DMF, after which a fivefold molar excess of $MnCl_4 \cdot 4H_2O$ was added with continuous stirring. The mixture was heated to boil and then refluxed for 30–40 min. The conversion of the porphyrin into the complex was monitored spectrophotometrically by disappearance of the porphyrin bands from the electronic absorption spectrum of the reaction mixture. To isolate (Cl)Mn·OEP, we added chloroform and water to the cooled reaction mixture to obtain a two-phase system. The chloroform layer with the dissolved Mn complex was separated, washed with water to remove excess salt and DMF, partially evaporated, and chromatographed two times on a column with alumina (Brockmann grade II), using chloroform as eluent.

Electronic absorption spectrum of (Cl)MnOEP in $CHCl_3$ [$\lambda_{max}$, nm ($\log\varepsilon$)]: 357 (4.87), 428 (4.17), 473 (4.68), 559 (4.01), 590 (3.76), 687 (3.22), 787 (3.45). IR spectrum ($\nu$, $cm^{-1}$): 728, 749 $\gamma(C_\beta–C)$; 841 $\gamma(C_{meso}–H)$; 1055 $\delta(C_\beta–C)$; 962, 989, 1019, 1062, 1112, 1148, 1272 skeleton vibrations of the macroring; 1315 $\nu(C–N)$; 1373, 1451, 1464, 1480 $\delta(CH_3)$, $\delta(CH_2)$; 1604, 1632 skeleton vibrations of pyrrole rings; 2931 $\nu(CH_2)$; 2872, 2966 $\nu(CH_3)$. The electronic absorption spectra were recorded on Hitachi U-2000, Specord M-40, and SF-26 spectrophotometers, and the IR spectra, on Specord IR-80 and Avatar 360 FT-IR spectrometers (KBr pellets).

The kinetics of the reaction of (Cl)MnOEP with $H_2O_2$ in $H_2O$–DMF was studied specrophotometrically in the temperature range 288–308 K. The optical density of the solutions in the course of the reaction was measured at $\lambda$ = 458 nm. The solutions were thermostated for 10 min before the measurements; the temperature fluctuations in the cell did not exceed $\pm 0.1$°C.

DMF of chemically pure grade was vacuum-distilled before use. The initial $H_2O_2$ concentration in water ($17.4 \pm 0.1$ M) was determined by iodometric titration.

The apparent reaction constants $k_{app}$ were optimized by least-squares treatment of the $\ln(C^0/C^\tau)$–$\tau$ dependences, and the true reaction constants $k$ and reaction orders $n$ were evaluated from the $\log k_{app}$–$\log C_{H_2O_2}$ dependences. The activation energies $E'$ and $E$ were determined from the slopes of the straight lines in the coordinates $\log k_{app}$–$1/T$ and $\log k$–$1/T$, respectively; the activation entropies $\Delta S^{\neq'}$ and $\Delta S^{\neq}$ were calculated by formula (22) [4]:

$$\Delta S^{\neq} = 19.1\log k^T + E/T - 19.1\log T - 205. \quad (22)$$

The equilibrium constant of the reaction of (Cl)·MnOEP with hydrogen peroxide was calculated by Eq. (22) using the least-squares method:

$$K = \frac{(A_{eq} - A_0)/(A_\infty - A_0)}{1 - (A_{eq} - A_0)/(A_\infty - A_0)} \times \frac{1}{[C^0_{H_2O_2} - C^0_{(Cl)MnOEP}(A_{eq} - A_0)/(A_\infty - A_0)]^{1/2}}, \quad (23)$$

where $A_0$, $A_\infty$, and $A_{eq}$ are the optical densities of the solutions of the starting compound, complex with $H_2O_2$, and their equilibrium mixture at the working wavelength.

The calculations were performed using Origin 61 and Microsoft Excel programs.

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