ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 5, pp. 1011–1017. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © T.N. Lomova, M.V. Klyuev, E.N. Ovchenkova, M.E. Klyueva, 2010, published in Zhurnal Obshchei Khimii, 2010, Vol. 80, No. 5, pp. 841–847.

Kinetics and Mechanism of Decomposition of Hydrogen Peroxide in the Presence of Manganese(III) Porphyrins

T. N. Lomova[a], M. V. Klyuev[b], E. N. Ovchenkova[a], and M. E. Klyueva[c]

[a] *Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
e-mail: tnl@isc-ras.ru

[b] *Ivanovo State University, Ivanovo, Russia*

[c] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*

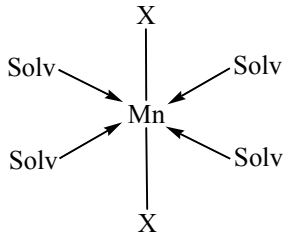
Received July 20, 2007

Abstract—The kinetics of homogeneous decomposition of hydrogen peroxide in the presence of manganese complexes with anionic ligands and various aromatic macrocycles were studied by the volumetric method. Ion–molecular mechanism was proposed on the basis of spectrophotometric data for catalytic decomposition of hydrogen peroxide with participation of manganese(III) porphyrins. The catalytic activity of the porphyrin complexes was higher by a factor of 1.5–3 than the activity of the corresponding solvate complexes with anionic ligands. The catalytic activity of porphyrin manganese complexes can be controlled by variation of the electronic structure of the macroring and the nature of anionic ligand coordinated at the apical position.

DOI: 10.1134/S1070363210050270

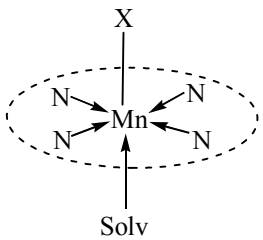
Interest in studying catalytic activity of manganese coordination compounds is related to their important role in biological processes as components of manganese-containing catalases [1–3] and in photosynthesis (photosystem II) [1–5], as well as to the unique ability of manganese ion to readily change its oxidation state from +2 to +7. The catalytic activity of manganese complexes in the decomposition of hydrogen peroxide was the subject of numerous studies [1, 6–8]; in particular, manganese complexes with porphyrins and phthalocyanines were examined. It was found that monomeric and covalently bonded dimeric manganese porphyrins exhibit catalase activity in the presence of imidazole under conditions of phase-transfer catalysis [9]. However, the composition and stability of the catalytically active complex, as well as the mechanism of decomposition of hydrogen peroxide, remain poorly studied.

In the present work we compared the catalytic activities of manganese(II) and manganese(III) complexes **I**–**V** with anionic ligands and various aromatic macrocycles, as well as of free tetraphenylporphyrin (**VI**), in the decomposition of hydrogen peroxide.



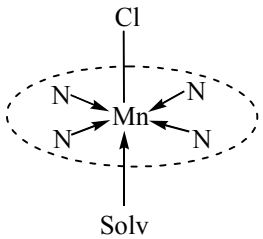
I, II

Solvate Mn^{II} complexes $[MnX_2Solv_4]$
I, X = Cl; **II**, X = OAc



III, IV

meso-Tetraphenylporphyrinatomanganese(III) [(X)MnTPP]
III, X = Cl; **IV**, X = OAc



V

Mono(meso-phenyl)-β-octamethylporphyrinatomanganese(III)

Table 1. Rates of hydrogen peroxide decomposition (W) and catalytic activities (A[a]) at different catalyst concetrations; $c(H_2O_2)$ = 3.98, c(KOH) = 1.9×10^{-2} M, 343 K

Catalyst	$c_{cat}\times10^5$, M	W, ml O_2/min	A, s^{-1}
–	–	0.8±0.2	–
V	0.13	1.2±0.1	55±3
	0.38	1.5±0.2	23±2
	1.05	2.1±0.4	12±2
	2.11	3.5±0.3	9±1
III	0.81	1.5±0.1	11±1
	2.25	1.7±0.2	4.5±0.5
	8.05	2.3±0.3	1.8±0.3
	11.60	2.6±0.1	1.3±0.1
IV	0.40	1.0±0.1	14.0±1.5
	0.80	1.2±0.1	9.1±0.5
	3.98	1.4±0.2	2.0±0.4
	7.96	1.7±0.2	1.3±0.2
$MnCl_2$	0.60	1.26±0.04	12.4±0.4
	1.43	1.3±0.1	5.5±0.5
	5.95	1.4±0.3	1.5±0.3
	11.90	1.7±0.2	0.8±0.1
$Mn(OAc)_2$	0.62	1.0±0.1	9.6±1.0
	1.27	1.2±0.1	5.5±0.5
	6.20	1.4±0.1	1.3±0.1
	12.70	1.52±0.07	0.70±0.04
VI	0.85	1.1±0.1	
	1.69	1.1±0.1	
	8.45	1.1±0.1	
	16.90	1.00±0.02	

[a] $A = W/c_{cat}$.

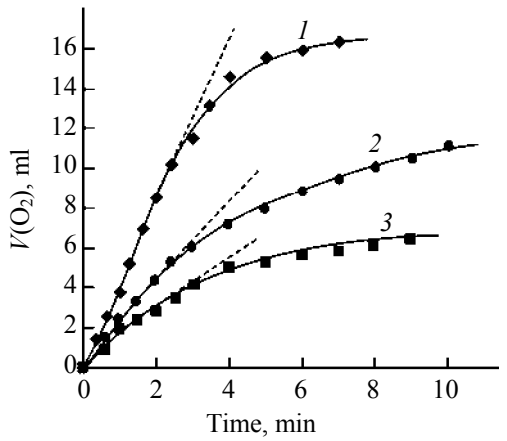


Fig. 1. Plots of the volume of liberated oxygen versus time in the decomposition of hydrogen peroxide in the presence of complexes **III**–**V**; $c(H_2O_2)$ = 3.98, c(KOH) = 9×10^{-2} M, 343 K; (*1*) $c_{\mathbf{V}} = 2.11\times10^{-5}$, (*2*) $c_{\mathbf{III}} = 0.80\times10^{-5}$, (*3*) $c_{\mathbf{IV}} = 0.80\times10^{-5}$ M.

Table 2. Rates of hydrogen peroxide decomposition (W) and catalytic activities (A) of complexes **III** and **IV** at different concetrations of hydrogen peroxide;. $c_{\mathbf{IV}} = 0.8\times10^{-4}$, c(KOH) = 1.9×10^{-2} M; $c_{\mathbf{III}} = 0.47\times10^{-4}$, c(KOH) = 1.5×10^{-2} M; 343 K

Comp. no.	$c(H_2O_2)$, M	W, ml O_2/min	A, s^{-1}
IV	1.99	0.76±0.04	5.6±0.3
	2.98	1.01±0.05	7.5±0.3
	3.98	1.23±0.07	9.1±0.5
	4.98	1.5±0.1	11.3±1.0
III	1.99	0.59±0.02	7.4±0.2
	2.98	0.94±0.04	11.8±0.5
	3.98	1.58±0.05	19.8±0.6
	4.98	1.9±0.1	23.8±1.6

The reaction under study is an example of homogeneous process. The substrate, hydrogen peroxide, resides in aqueous–organic phase, where manganese complex and potassium hydroxide are also dissolved. No decomposition of hydrogen peroxide occurred in analogous system in the absence of KOH. The rate constant for the decomposition of hydrogen peroxide is formally zero-order with respect to oxygen (Fig. 1; Tables 1–3), and it increases as the concentration of manganese complex, KOH, and H_2O_2 rises provided that the two latter are present in considerable excess with respect to the manganese complex. The fact that the reaction rate remains constant upon variation of the concentration of compound **VI** and its insignificant difference from the reaction rate observed in the absence of **VI** indicated the lack of catalytic activity of free *meso*-tetraphenylporphyrin **VI**.

Porphyrin manganese(III) complexes showed an appreciable catalase activity (Tables 1–3); they accelerated the process and reduced its energy of activation (Table 4). For example, complex **IV** reduced the effective energy of activation by a factor of more than 5 (from 73 to 14 kJ mol^{-1}), and complex **III**, by a factor of 1.5 (to 37 kJ mol^{-1}). Solvate complexes MnX_2 (**I**, **II**) also exhibited catalytic activity.

Treatment of the $\log W$—$\log c$ dependences for hydrogen peroxide (R^2 = 0.98) and hydroxide ion (R^2 = 0.99) indicated that the order of the reaction in these components is close to unity. The first order in the catalyst followed from the linear dependence W—c_{cat} for all experimental points except one corresponding to the lowest concentration of complex **IV** (Fig. 2).

The rate constants k_{343} (at 343 K) in the presence of complex **III** [$(1.2\pm0.1)\times10^5$, $(2.6\pm0.1)\times10^5$, and

Table 3. Rates of hydrogen peroxide decomposition (W) and catalytic activity (A) of complex **III** at different potassium hydroxide concentrations; $c_{\mathbf{III}} = 0.47\times10^{-4}$, $c(H_2O_2) = 3.98$ M, 343 K

c_{KOH}, M	W, ml O_2/min	A, s^{-1}
0.044	1.75±0.05	21.9±0.6
0.044	1.59±0.05	19.8±0.6
0.055	1.9±0.1	24.0±1.2
0.066	2.4±0.2	30.0±2.1
0.077	1.89±0.06	23.7±0.7
0.088	3.6±0.2	45.3±2.5

1.34×10^5 ml O_2 l^3 mol^{-3} min^{-1}; $R^2 = 0.996$] were calculated from the data obtained in three independent experiments with variation of the KOH, H_2O_2, and catalyst concentration, respectively. Analogous values, $(2.95\pm0.04)\times10^5$ and 1.10×10^5 ml O_2 l^3 mol^{-3} min^{-1} ($R^2 = 0.95$), were obtained for the reaction in the presence of complex **IV** from the data of two experiments with variation of the H_2O_2 and catalyst concentration. Using the above values, we calculated the simple average rate constants k_{343} for hydrogen peroxide decomposition in the presence of complexes **III** and **IV**: $(1.72\pm0.6)\times10^5$ ml O_2 l^3 mol^{-3} min^{-1} [(0.12 ± 0.04) l^3 mol^{-2} s^{-1}] and $(2.0\pm0.9)\times10^5$ ml O_2 l^3 mol^{-3} min^{-1} [(0.14 ± 0.06) l^3 mol^{-2} s^{-1}], respectively.

Taking into account zero order of the reaction with respect to oxygen, the experimental reaction rate is given by Eq. (1).

$$\partial c_{O2}/\partial\tau = k\cdot c_{cat}\cdot c_{H2O2}\cdot c_{OH^-}\cdot c^0_{O2} = k\cdot c_{cat}\cdot c_{H2O2}\cdot c_{OH^-}. \quad (1)$$

Spectrophotometric study on the reaction of complex **III** with hydrogen peroxide H_2O_2 in aqueous dimethylformamide revealed the following. At low concentration of hydrogen peroxide (0.017–0.5 M) in a solution of complex **III** in DMF, the intensity of the characteristic charge-transfer band of complex **III** at λ 467 nm decreases with time, and a new absorption band appears with its maximum at λ 679 nm. This band belongs to the π-radical cation form of complex **III** (oxidized at the macroring) [10]. In the range of H_2O_2 concentration from 0.5 to 2 M, the intensity of absorption bands at λ 467 and 679 nm decreases, while absorbance in the region λ 486–599 nm, typical of manganese(IV) porphyrins [11, 12] increases. In the hydrogen peroxide concentration range 2–3.98 M the transformation of Mn^{III}TPP into Mn^{IV}TPP is observed directly (Fig. 3). Analogous $Mn^{III}\rightarrow Mn^{IV}$ transformation

Table 4. Rates of hydrogen peroxide decomposition (W) and catalytic activities (A) of complexes **III** and **IV** at different temperatures; initial concentrations: $c(H_2O_2) = 3.98$, $c(KOH) = 1.9\times10^{-2}$, $c_{\mathbf{IV}} = 0.8\times10^{-5}$, $c_{\mathbf{III}} = 0.47\times10^{-5}$ M

Catalyst	T, K	W, ml O_2/min	A, s^{-1}	E, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
None	343	0.60±0.02	–	73±7	–42±20
	353	1.7±0.2	–		
	363	3.2±0.3	–		
IV	343	1.23±0.07	9.1±0.5	14±1	–210±3
	353	1.4±0.1	11±1		
	363	1.6±0.2	12.5±1.5		
III	343	1.44±0.04	18.1±0.5	37±2	–141±6
	353	2.33±0.07	28.5±0.8		
	363	3.2±0.2	38±2		

was described previously by Haruta et al. [13] who studied catalysis of hydrogen peroxide decomposition by dimeric porphyrins [13]. Thus the results of studying the reaction of H_2O_2 with complex **III** in the absence of alkali demonstrate the possibility for transitions between Mn^{III} and Mn^{IV} complexes, as well as fairly high stability of manganese porphyrins toward H_2O_2.

Taking into account the above stated, the process of catalytic decomposition of hydrogen peroxide in the presence of manganese porphyrin complexes may be represented by reactions (2)–(5).

$$H_2O_2 + OH^- \overset{K_1}{\rightleftharpoons} HO_2^- + H_2O, \quad (2)$$

$$(Cl)Mn^{III}TPP + HO_2^- \xrightarrow[\text{fast}]{k_2} (Cl)(HO_2^-)Mn^{III}TPP, \quad (3)$$

$$(Cl)(HO_2^-)Mn^{III}TPP \xrightarrow[\text{fast}]{k_3} O{=}Mn^{IV}TPP + Cl^- + OH^-, \quad (4)$$

$$O{=}Mn^{IV}TPP + HO_2^- \xrightarrow[\text{slow}]{k_4} (OH)Mn^{III}TPP + O_2. \quad (5)$$

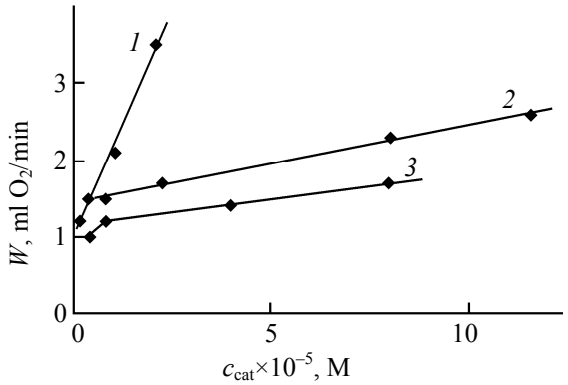


Fig. 2. Plots of the rate constant of hydrogen peroxide decomposition versus concentration of complexes (*1*) **V**, (*2*) **III**, and (*3*) **IV**; $c(H_2O_2) = 3.98$, $c(KOH) = 1.9\times10^{-2}$ M, 343 K. $R^2 = 0.96$–0.98.

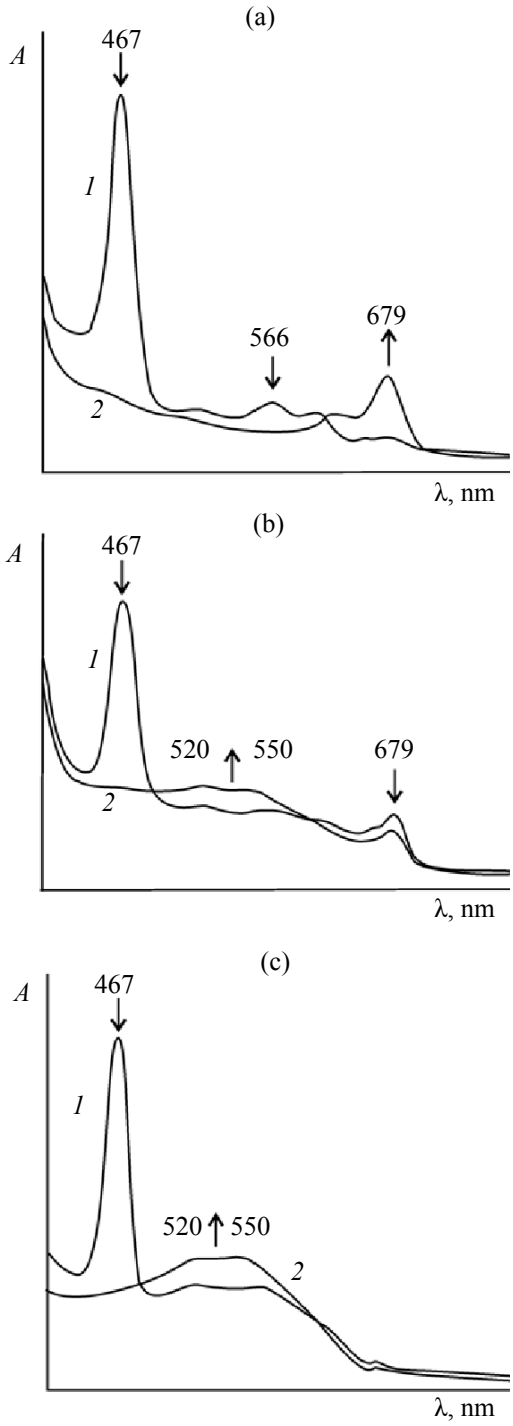


Fig. 3. (*1*) Initial and (*2*) final electronic absorption spectra of complex **III** after treatment with hydrogen peroxide in DMF–H_2O at 298 K, $c(H_2O_2)$, M: (a) 0.017, (b) 1.0, (c) 2.52.

The rate-determining step [reaction (5)] may be described by kinetic equation (6).

$$-\partial c(HO_2^-)/\partial\tau = \partial c(O_2)/\partial\tau = k_4\, c(O{=}Mn^{IV}TPP)c(HO_2^-). \quad (6)$$

Substituting the expression for $c(HO_2^-)$ [$c(HO_2^-) = K_1 \cdot c(H_2O_2) \cdot c(OH^-)$] and taking into consideration that the concentration of Mn^{IV} complex is equal to the concentration of the initial Mn^{III} complex [$c(H_2O_2) > 1.99$ M] gives Eq. (7) for the rate constant k. Using Eq. (7) we can determine the rate constant for the rate-determining step [reaction (5)] provided that the equilibrium constant K_1 [equilibrium (2)] is known.

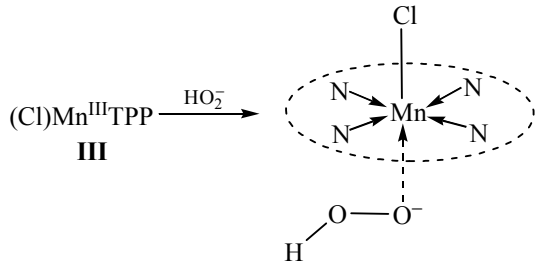
$$k = k_4 K_1. \quad (7)$$

The proposed ion–molecular mechanism is confirmed by the experimental and published data. First, fast trans-formation of $(Cl)Mn^{III}TPP$ into $O{=}Mn^{IV}TPP$ in the course of H_2O_2 decomposition [$c(H_2O_2) = 2$–5 M] is observed experimentally (Fig. 3). Second, Cheremen-skaya et al. [9] also reported on increase in the rate of decomposition of hydrogen peroxide with rise in the concentrations of the catalyst [manganese(III) complexes with tetraphenylmethoxy-porphyrin and hematoporphyrin] and base (imidazole). Finally, the electronic absorption spectrum of the reaction mixture, recorded after the evolution of gaseous products was complete, was typical of (tetra-phenylporphyrinato)manganese(III): it characteristically contained an absorption band at about 470 nm. Simultaneously, some reduction in the concentration of metal porphyrin and appreciable increase of the intensity of "benzene" absorption in the UV region were observed due to partial decomposition of the macrocyclic ligand.

It should be noted that decomposition of hydrogen peroxide was studied at low substrate conversion, and the reaction mixture contained a considerable amount of unchanged hydrogen peroxide (90%), which was confirmed by iodometric titration. The conversion attained in [9] was higher, presumably due to larger amount of the catalyst: the substrate-to-catalyst ratio was 2×10^2 [9] against $(1–5)\times10^6$ in our study. Therefore, the fact that the reaction was complete despite the presence of unchanged H_2O_2 may be rationalized in terms of decomposition of the catalyst. Furthermore, assuming that one-electron oxidation of complex **III** at the central metal ion [reaction (4)] involves coordination of hydrogen peroxide as HO_2^- ion at the apical position *6* (Scheme 1), replacement of electron-donor DMF or H_2O molecule in the initial complex **III** (dissolved in DMFA–H_2O) is necessary. Thus the second step [reaction (3)] slows down as hydrogen peroxide is consumed.

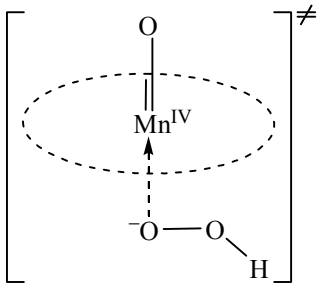
The proposed stepwise mechanism is consistent with the ratio of the activation parameters of the

Scheme 1.



catalytic process (Table 4). Sharp reduction in the effective energy of activation of hydrogen peroxide decomposition in the presence of porphyrin manganese complexes is likely to result from decrease in energy consumption due to formation of polar transition state $[O{=}Mn^{IV}TPP{\cdot}HO_2^-]^{\neq}$ [Scheme (2)] in the rate-determining step [reaction (5)]. The assistance by solvation of transition state in the noncatalytic reaction [$\Delta S^{\neq}$ = (–42±20) J mol^{-1} K^{-1}] is different from that in the reaction catalyzed by manganese tetraphenylporphyrins, where $\Delta S^{\neq}$ = (–141±6) J mol^{-1} K^{-1} for complex **III** and $\Delta S^{\neq}$ = (–210±3) J mol^{-1} K^{-1} for complex **IV**.

Scheme 2.



As follows from the data in Table 1, the catalytic activity of complex **V** is twice as high as that of **III** and is higher by a factor of 2–3 than that of $MnCl_2$. High catalytic activity of complex **V** suggests that the porphyrin ligand considerably affects the catalytic process. Using compound **VI** as an example we showed (Table 1) that free *meso*-tetraphenylporphyrin exhibits no catalytic activity. Thus the role of coordinated macrocyclic ligand is to change the electron density on the central metal ion, which is consistent with the assumed initial coordination of H_2O_2 to porphyrin manganese(III) complex. The electron density on the manganese atom in complex **V** is higher than in complex **III** due to electron-donating effect of eight methyl groups and elimination of electron-withdrawing effect of three phenyl group. Taking into account ligand *trans* influence [14], the coordination bond between anionic ligand (chloride ion) in the apical position and the metal ion should weaken, thus facilitating coordination of hydrogen peroxide at the other apical position (*trans*). Chugreev et al. [15] showed that the presence of electron-donating *p*-methoxyphenyl substituents in the *meso* positions of the macroring increases the catalytic activity of porphyrin manganese complexes in the oxidation of cholesterol, as compared to analogous derivatives having the same substituents in the pyrrole rings. Presumably, this is the result of change in the geometric parameters of the coordination entity (shortening of the distance from the metal ion to the centroid of the plane formed by the four coordinating nitrogen atoms), which should also favor coordination at the apical position.

The data in Table 1 suggest a complicated relation between the catalytic activities of complexes **III** and **IV**, specifically the catalytic activity weakly depends on the nature of anionic ligand provided that the concentrations of hydrogen peroxide and potassium hydroxide are constant, but it is appreciably higher for complex **III** [provided that c_{cat} and c(KOH) are constant).

Spectrophotometric study on the reaction of complex **IV** with hydrogen peroxide (cf. the data shown in Fig. 3 for complex **III**) showed that the transformation of complex **IV** into the corresponding oxidized state is more facile. Thus the lack of distinct relation between the catalytic activity of $(X)Mn^{III}TPP$ and the nature of anionic ligand X confirms the scheme represented by reactions (2)–(5), where ligand X is not present in the coordination sphere at the rate-determining step (5).

To conclude, we can state that the catalytic decomposition of hydrogen peroxide in the presence of porphyrin manganese(III) complexes follows a ionic–molecular mechanism and that that the catalytic activity of manganese complexes can be controlled by varying the electronic structure of the macrocyclic ligand.

EXPERIMENTAL

The electronic absorption spectra of metal porphyrins and products of their oxidation with hydrogen peroxide were recorded on Specord M-40 and Hitachi U 2000 spectrophotometers.

Complexes **III** and **IV** were synthesized from the corresponding porphyrin and manganese salt

($MnCl_2 \cdot 4H_2O$ or $Mn(OAc)_2 \cdot 4H_2O$ of analytical grade) according to Adler [16]. The complexes were identified, and their purity was determined, by the electronic absorption spectra in chloroform, λ_{max} ($\log\varepsilon$), nm: **III**: 402 (4.64), 478 (4.98), 524 (3.81), 582 (4.00), 616 (3.03); **IV**: 403 (3.61), 427 (3.48), 480 (4.98), 527 (3.70), 584 (3.94), 618 (3.97) [17]; **V**: 420 (4.21), 476 (4.54), 566 (4.01), 596 sh [18].

Decomposition of hydrogen peroxide was studied in the system DMF–KOH–H_2O at 343–363 K in a jacketed reactor equipped with a magnetic stirrer. The reactions were carried out under vigorous stirring. The concentrations of the complex and potassium hydroxide were varied by taking their required amounts; 1 ml of an aqueous solution of KOH and 2 ml of an aqueous solution of hydrogen peroxide, $c(H_2O_2)$ = (19.9±0.2) M were added to 7 ml of a solution of the corresponding complex in DMF. The concentration of H_2O_2 was varied by diluting its aqueous solution to a volume of 1–2.5 ml; correspondingly, the volume of DMF was varied to attain an overall volume of the reaction mixture of 10 ml. The initial concentration of hydrogen peroxide in water (19.9±0.2) M was determined by iodometric titration. The reaction rate was measured by volumetry on the basis of the volume of liberated oxygen.

The rates of hydrogen peroxide decomposition W, which were equal to the effective formal zero-order rate constants k_{eff}^{T} (Tables 1–3), were determined as the slope of the linear part of the $V(O_2)$–τ dependence (Fig. 1). The catalytic activity A was calculated by dividing W (expressed in the International System of Units) by the catalyst concentration (in mol l^{-1}). The energy of activation E was determined by optimizing the linear dependence $\log k_{eff}^{T}$—$1/T$ by the least squares procedure. The entropy of activation ($\Delta S^{\neq}$) was calculated using the base equation of the transition state theory, reduced to form (8) [19].

$$\Delta S^{\neq} = 19.1\log k_{eff}^{T} + E/T - 19.1\log T - 205. \quad (8)$$

Here, k_{eff}^{T} is the formal zero-order rate constant at a temperature T. The true rate constants and orders of the reaction (n) with respect to H_2O_2 and OH^- were determined by plotting the log dependences of the rate constants versus concentration, and the order with respect to the catalyst was determined from the dependence of W upon catalyst concentration. The calculations were performed using Origin 61 and Microsoft Excel.

ACKNOWLEDGMENTS

This study was performed under financial support in part by the Presidium of the Russian Academy of Sciences (program no. 18, "Development of Methods for the Preparation of Chemical Substances and Design of New Materials"), by the Ministry of Education and Science of the Russian Federation (branch target program "Development of Scientific Potential at Higher School," project no. 2.2.1.1/2820, and by the Russian Foundation for Basic Research (project no. 07-03-00639).

REFERENCES

1. Khangulov, S.V., Barynin, V.V., Melik-Adomyan, V.R., Grebenko, A.N., Voevodskaya, N.V., Blyumenfel'd, L.A., Dobryakov, S.N., and Il'yasova, V.B., *Bioorg. Khim*., 1986, vol. 12, no. 6, p. 741.
2. Khangulov, S.V., Voevodskaya, N.V., Barynin, V.V., Grebenko, A.I., and Melik-Adomyan, V.R., *Biofizika*, 1987, vol. 32, no. 6, p. 960.
3. Dismukes, G.S., *Chem. Rev*., 1996, vol. 96, no. 7, p. 2909.
4. Rüttinger, W. and Dismukes, G.C., *Chem. Rev*., 1997, vol. 97, no. 1, p. 1.
5. Yachandra, V.K., Sauer, K., and Klein, M.P., *Chem. Rev*., 1996, vol. 96, no. 7, p. 2927.
6. Batyr, D.G., Isak, V.G., Kirienko, A.A., and Kharitonov, Yu.Ya., *Koord. Khim*., 1986, vol. 12, no. 4, p. 435.
7. Sychev, A.Ya., Isak, V.G., and Fyong, Ch.T.T., *Zh. Fiz. Khim*., 1984, vol. 58, no. 2, p. 332.
8. Sychev, A.S. and Isak, V.G., *Usp. Khim*., 1993, vol. 62, no. 3, p. 303.
9. Cheremenskaya, O.V., Solov'eva, A.B., Ponomarev, G.V., and Timashev, S.F., *Zh. Fiz. Khim*., 2001, vol. 75, no. 10, p. 1787.
10. Kaustov, L., Tal, M.E., Shames, A.I., and Gross, Z., *Inorg. Chem*., 1997, vol. 36, no. 16, p. 3503.
11. Carnieri, N., Harriman, A., Porter, G., and Kalyanasundaram, K., *J. Chem.. Soc., Dalton Trans*., 1982, p. 1231.
12. Volz, H. and Müller, W., *Chem. Ber*., 1997, vol. 130, no. 8, p. 1099.
13. Naruta, Y., Sasayama, M., and Ichihara, K., *Russ. J. Org. Chem*., 1996, vol. 32, no. 2, p. 214.
14. Grinberg, A.A., *Vvedenie v khimiyu kompleksnykh soedinenii* (Introduction to the Chemistry of Coordination Compounds), Moscow: Khimiya, 1966.

15. Chugreev, V.L., Solov'eva, A.B., Misurkin, I.A., and Samokhvalova, A.I., *Teor. Eksp. Khim*., 1987, no. 4, p. 428.

16. Adler, A D., Longo, F.R., Kampas, F., and Kim, J., *J. Inorg. Nucl. Chem*., 1970, vol. 32, p. 2443.

17. Lomova, T N., Volkova, N.I., and Berezin, B.D., *Zh. Neorg. Khim*., 1985, vol. 30, no. 4, p. 935.

18. Klyueva, M E. and Lomova, T.N., *Mendeleev Commun*., 2003, vol. 12, no. 6, p. 238.

19. Lomova, T.N., *Doctoral (Chem.) Dissertation*, Ivanovo, 1990.