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CHEMICAL KINETICS
AND CATALYSIS

The Kinetics of Disproportionation of Hydrogen Peroxide in the Presence of Palladium(II)porphyrins with Regularly Changing Macroring Structures

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Abstract—The kinetics and spectral manifestations of alkaline decomposition of H_2O_2 in a water–dimethylformamide medium catalyzed by $Pd^{II}P$ (P is the dianion of octaethylporphyrin and its monophenyl, 5,15-diphenyl, 5,10-diphenyl, triphenyl, and tetraphenyl derivatives substituted at meso positions) was studied over a wide range of reagent concentrations under polythermal conditions. A complete kinetic description of the reacting systems was given, and the rates and set of elementary reactions, intermediate compounds, and kinetically significant equilibria were determined. The ion-molecular mechanism of hydrogen peroxide decomposition was substantiated. According to this mechanism, the only stable radicals involved in the reaction are the π radical cation forms of palladium(II)porphyhrin catalysts.

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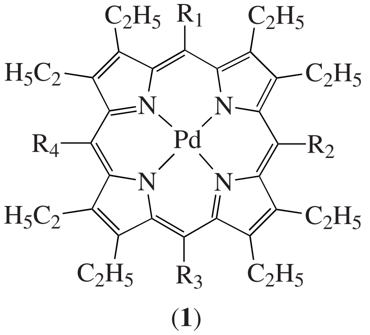
INTRODUCTION

The chemistry of palladium largely includes square planar complex compounds [1]. The catalytic properties of Pd complexes are based on their ability to participate in weak axial interactions. According to the critically selected sample of data on 10000 metal compounds, there are 380 Pd compounds with the coordination number (CN) four and only four and seven compounds with CN = 5 and 6, respectively [2]. The catalytic decomposition of H_2O_2 was studied using palladium tetrapyrrole complexes with monomeric and polymeric phthalocyanines, which had moderate catalytic effects [3]. Because of strengthening of π interactions in porphyrin (PdP) compared with phthalocyanine (PdPc) complexes, both within the square coordination sphere PdN_4 and in axial directions, and the possibility of controlling them by modifying the porphyrin macroring, studies of PdP are of importance for seeking effective synthetic catalases and open up many possibilities for investigating the mechanism of decomposition of H_2O_2.

The purpose of this work was to study the catalytic properties of palladium(II)octaethylporphyrins (**1**) with step phenyl substitution (up to exhaustive) at the meso porphyrin ligand positions in the decomposition of hydrogen peroxide,



(**1**)

PdOEP, $R_1 = R_2 = R_3 = R_4 = H$,
PdMPOEP, $R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$,
$Pd^{5,15}$DPOEP, $R_1 = R_3 = C_6H_5$, $R_2 = R_4 = H$,
$Pd^{5,10}$DPOEP, $R_1 = R_2 = C_6H_5$, $R_3 = R_4 = H$,
PdTrPOEP, $R_1 = R_2 = R_3 = C_6H_5$, $R_4 = H$,
PdTetPOEP, $R_1 = R_2 = R_3 = R_4 = C_6H_5$;

$$2H_2O_2 \longrightarrow H_2O + O_2\uparrow. \qquad (1)$$

EXPERIMENTAL

Complexes **1** were synthesized in reactions between the corresponding porphyrin and $PdCl_2$ in dimethylformamide (DMFA), purified, identified [4], and kindly provided to us by A.S. Semeikin (Ivanovo State University of Chemical Technology). The electronic absorption spectra (350–700 nm, l = 1.000 cm, 298 K) of PdP were recorded on Specord M-40 and Hitachi U 2000 spectrophotometers.

The decomposition of H_2O_2 of reagent grade in the presence of complexes **1** was studied in the DMFA (kh. ch. (chemically pure))–KOH (kh. ch.)–H_2O (doubly distilled) system at 343–363 K and atmospheric pressure in a temperature-controlled reactor under continuous stirring conditions. An aqueous solution of H_2O_2 (18.1 ± 0.2 mol/l) titrated iodometrically was added to a solution of a Pd complex and KOH in DMFA. The concentrations of complexes **1**, KOH, and H_2O_2 were varied over the ranges 10^{-6}–10^{-4}, 0.0018–0.036, and 0.9–7.22 mol/l, respectively. The rate of the reaction W was determined volumetrically, by measuring the volume of oxygen released (Tables 1, 2). The W and catalytic activity A ($A = W/c_{PdP}$) values were determined from the slope of the linear portion of the V_{O_2}–τ dependence optimized by the method of least squares (Microsoft Excel) with respect to the positive direction of the abscissa axis. Reaction orders (n) with respect to H_2O_2 and KOH were determined by optimizing the linear dependences of $\log W$ on the logarithm of the concentration of the corresponding component, the concentrations of the other reaction participants being constant (Fig. 1). The activation energy of the reaction E was determined from the slope of the straight line in the coordinates $\log W$ versus $1/T$ (Table 3). The entropy of activation was calculated using the main equation of transition state theory [6] written as

$$\Delta S^{\neq} = 19.1\log W + \frac{E \pm \Delta E}{T} - 19.1\log T - 205, \quad (2)$$

where ΔE is the root-mean-square deviation and T is the temperature.

RESULTS AND DISCUSSION

We see from Table 2 and Fig. 1 that W increases as the concentrations of KOH and H_2O_2 grow. In all cases, there is a satisfactory linear correlation between the logarithm of W and the concentration of OH^- with a slope close to one.

According to the $\log W - \log c_{H_2O_2}$ dependences (Fig. 1), the order of the reaction with respect to hydrogen peroxide changes from 1.2 to 1.6 depending on the Pd complex used. The correlation coefficient, however, sharply increases if the whole $c_{H_2O_2}$ range is divided into two regions, 0.9–3.6 and 3.6–7.2 mol/l H_2O_2 (Fig. 1), for which the order of the reaction in $c_{H_2O_2}$ is close to 1 and 2, respectively.

Table 1. Rate of decomposition of H_2O_2 (W) and catalytic activity (A) of palladium(II)porphyrins at various catalyst concentrations, T = 343 K, $c_{H_2O_2}$ = 3.61 mol/l, and c_{KOH} = 0.018 mol/l

Complex	$c_{PdP} \times 10^5$, mol/l	W, ml O_2/min	A, s^{-1}
No catalyst	–	0.8 ± 0.1	–
PdOEP	0.215	2.00 ± 0.07	55 ± 2
	2.15	2.20 ± 0.17	6.0 ± 0.5
	10.8	2.93 ± 0.40	1.60 ± 0.02
PdMPOEP	0.282	1.52 ± 0.06	32 ± 1
	2.82	1.59 ± 0.09	3.3 ± 0.2
	14.1	1.53 ± 0.14	0.64 ± 0.06
$Pd^{5,15}$DPOEP	0.34	1.53 ± 0.14	27 ± 2
	3.40	1.56 ± 0.11	2.7 ± 0.2
	13.6	1.82 ± 0.14	0.80 ± 0.06
$Pd^{5,10}$DPOEP	0.29	1.41 ± 0.04	29 ± 1
	2.90	1.51 ± 0.06	3.0 ± 0.1
	14.5	1.72 ± 0.09	0.70 ± 0.04
PdTrPOEP	0.28	1.45 ± 0.07	31 ± 2
	2.80	1.40 ± 0.09	3.0 ± 0.2
	14.0	1.42 ± 0.12	0.60 ± 0.05
PdTetPOEP	0.21	1.51 ± 0.08	43 ± 2
	2.10	1.63 ± 0.07	4.6 ± 0.2
	12.6	1.95 ± 0.10	0.90 ± 0.05

Table 2. Rate of decomposition of H_2O_2 (W) and catalytic activity of palladium(II)porphyrins (I, PdOEP, $c_{PdP} = 2.15 \times 10^{-5}$ mol/l, and II, PdTrPOEP $c_{PdP} = 2.80 \times 10^{-5}$ mol/l) at various KOH concentrations, T = 343 K and $c_{H_2O_2}$ = 3.61 mol/l

c_{KOH}, mol/l	W, ml O_2/min		A, s^{-1}	
	I	II	I	II
0.0018	0.37 ± 0.02	0.42 ± 0.01	1.00 ± 0.05	0.90 ± 0.02
0.018	2.20 ± 0.17	1.40 ± 0.09	6.0 ± 0.5	3.0 ± 0.2
0.036	3.58 ± 0.16	2.76 ± 0.07	9.9 ± 0.4	5.80 ± 0.15

The reaction order with respect to the concentration of the catalysts determined from the data presented in Table 1 for reactions catalyzed by the PdMPOEP and PdTrPOEP complexes is close to zero, and W is almost independent of c_{PdP}. With $Pd^{5,15}$DPOEP, $Pd^{5,10}$DPOEP, and PdTetPOEP, the order is insignificantly larger than 0 (0.02–0.05). With PdOEP, it increases to 0.09.

It follows that, according to the experimental data, the total kinetic equations for the intervals $c_{H_2O_2}$ = 0.9–3.6

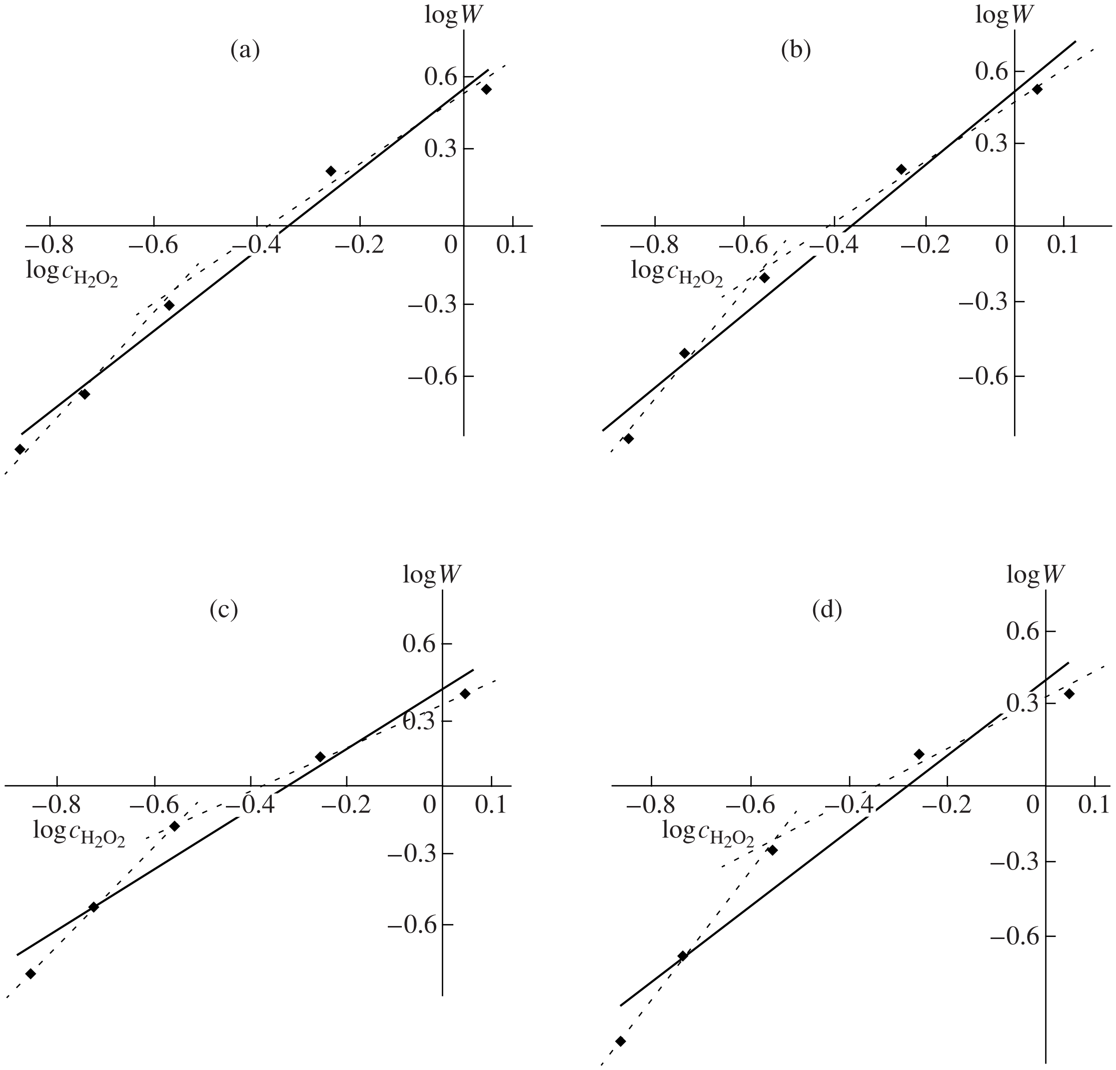


Fig. 1. Dependences of the logarithm of the rate of H_2O_2 decomposition on the logarithm of the concentration of H_2O_2 in the presence of (a) PdOEP, (b) PdMPOEP, (c) $Pd^{5,\,10}$DPOEP, and (d) PdTetPOEP; $c_{PdP} = 2.15 \times 10^{-5}$, 2.82×10^{-5}, 2.90×10^{-5}, and 2.10×10^{-5} mol/l, respectively; $c_{KOH} = 0.018$ mol/l, and $T = 343$ K; $R_2 = 0.992–0.999$.

and 3.6–7.2 mol/l can be written as

$$dc_{O_2}/d\tau = kc^0_{PdP}c_{H_2O_2}c_{KOH}c^0_{O_2} = kc_{H_2O_2}c_{KOH}, \quad (3)$$

$$dc_{O_2}/d\tau = k'c^0_{PdP}c^2_{H_2O_2}c_{KOH}c^0_{O_2} = k'c^2_{H_2O_2}c_{KOH}. \quad (4)$$

The mean rate constants k and k' for PdOEP at T = 343 K were found from two values for each constant determined in two independent experiments by optimizing the $\log W - \log c_{H_2O_2}$ and $\log W - \log c_{OH^-}$ dependences. They are 14.5 ± 1.8 ml O_2 l^2 min^{-1} mol^{-2} and 4.5 ± 0.9 ml O_2 l^3 min^{-1} mol^{-3}, respectively. For the other complexes, the k and k' constants (Table 4) were determined from the $\log W - \log c_{H_2O_2}$ dependences.

Zero reaction order with respect to PdP is evidence of a heterogeneous catalytic process. An insignificant increase in this value for PdOEP, whose initial concentration was lower than that of the other complexes, may mean the occurrence of a parallel reaction in the solution phase. It follows that, in the catalytic systems studied, homogeneous catalysis (with obvious predominance of heterogeneous catalysis) is only observed for the PdOEP catalyst. An increase in the order with respect to H_2O_2 as the concentration of H_2O_2 grows (Eqs. (3) and (4)) is in turn evidence that more than one H_2O_2 particle participates in the process. Before analyzing kinetic equations (3) and (4), let us consider the results of special spectral studies. The spectral properties of PdP–KOH, PdP–H_2O_2, and PdP–H_2O_2–KOH mixtures in mixed H_2O–DMFA solvents substantiate the conclusions made above. The electronic absorption spectra of solutions of PdP–KOH mixtures in water–dimethylformamide solvents contain unshifted PdP

Table 3. Rate of decomposition of H_2O_2 in the presence of palladium(II)porphyrins at 298 K, $c_{H_2O_2} = 3.61$ mol/l, and $c_{KOH} = 0.018$ mol/l and activation parameters E and $\Delta S^{\neq}$

Complex	W^{298}, ml O_2/min	A, s^{-1}	E, kJ/mol	$-\Delta S^{\neq}$, J/(mol K)
No catalyst	0.018 ± 0.004	–	72 ± 4	45 ± 12
PdOEP	0.26 ± 0.02	0.70 ± 0.05	40 ± 1	129 ± 3
PdMPOEP	0.163 ± 0.009	0.34 ± 0.02	43 ± 1	123 ± 3
$Pd^{5,15}$DPOEP	0.152 ± 0.016	0.26 ± 0.02	44 ± 2	120 ± 6
$Pd^{5,10}$DPOEP	0.128 ± 0.011	0.26 ± 0.02	47 ± 1	112 ± 3
PdTrPOEP	0.107 ± 0.008	0.23 ± 0.02	51 ± 1	100 ± 3
PdTetPOEP	0.090 ± 0.014	0.25 ± 0.04	55 ± 3	87 ± 10

Note: The W^{298} value was determined by the extrapolation of the dependences of W on 1/T, and the E and $\Delta S^{\neq}$ values were calculated in [5].

Table 4. Coefficients A and B of linear dependence (26) and rate constants k (calculated and experimental) and k_4 in Eqs. (3) and (8), respectively, for various palladium(II)porphyrins at 343 K

Complex	$A = k_4Kc^0_{OH^-}$	$B = -K$	$k_4 \times 10^{-2}$, ml O_2 l/(mol min)	k (k')	
				experimental	k_4K
PdOEP	0.373	−0.093	2.23	14.5 ± 1.8 (4.5 ± 0.9)	20.7
PdMPOEP	0.360	−0.098	2.04	18.1 (5.07)	20.0
$Pd^{5,10}$DPOEP	0.510	−0.146	1.94	24.3 (5.7)	28.4
PdTetPOEP	0.585	−0.171	1.89	29.2 (6.2)	32.4

Note: k and k' dimensionalities are ml O_2 l^2/(mol min) and ml O_2 l^3 min^{-1} mol^{-3}, respectively.

Table 5. Positions of bands (λ_{max}, nm) in the visible region of the electronic absorption spectra of palladium(II)porphyrins in DMFA, $CHCl_3$, and systems studied

Complex	DMFA	DMFA–KOH	DMFA–H_2O_2	DMFA–KOH–H_2O_2	$CHCl_3$
PdOEP	389, 508, 540	508, 541	508, 541	520, 555	392, 511, 545
PdMPOEP	402, 516, 549	516, 549	516, 549	529, 572	400, 516, 550
$Pd^{5,15}$DPOEP	406, 515, 548	515, 548	515, 548	529, 562	403, 517, 549
$Pd^{5,10}$DPOEP	415, 525, 559	525, 559	525, 559	531, 565	412, 527, 561
PdTrPOEP	425, 535, 570	535, 570	535, 570	539, 573	422, 536, 570
PdTetPOEP	436, 545, 581	545, 581	545, 581	549, 584	433, 544, 580

bands (Table 5), but the intensity of absorption decreases noticeably. We observe a decrease in the intensity of bands only (without noticeable band shifts) also for PdP–H_2O_2 mixtures (Table 5). Gas release is unnoticeable. Solutions are however unstable in time, they grow turbid, which is evidence of the precipitation of metalloporphyrins. In PdP–KOH–H_2O_2 systems, we observe gas release and the formation of precipitates. In the electronic absorption spectra of freshly prepared mixtures, when gas release is insignificant and there is no precipitate, the $Q(0, 0)$ and $Q(0, 1)$ absorption bands [7, 8] of the initial PdP complexes with maxima at 520–548 and 555–584 nm, respectively (Table 5), experience broadening and bathochromic shifts by 3–23 nm. We also observe an increase in overall absorption background and the appearance of absorption in the long-wave region and visible spectrum region adjacent to the UV range (Figs. 2a, 2b).

Such electronic absorption spectra are characteristic of π radical cation forms of metalloporphyrins obtained by chemical and electrochemical oxidation [9, 10]. Changes in the spectra of PdP in the PdP–DMFA–H_2O–KOH–H_2O_2 system compared with its solution in DMFA can therefore be explained by the formation of π radical cation forms $PdP^{+\bullet}$. According to [11], the π radical cation forms of metalloporphyrins are stable in solution but transform into the initial complex when their isolation from solutions is attempted. After gas release terminates, complexes from a solution of PdOEP and PdMPOEP and $Pd^{5,15}$DPOEP heterogeneous systems were isolated into $CHCl_3$, and these solutions were thoroughly washed from DMFA, KOH, and H_2O_2. The electronic absorption spectra of solu-

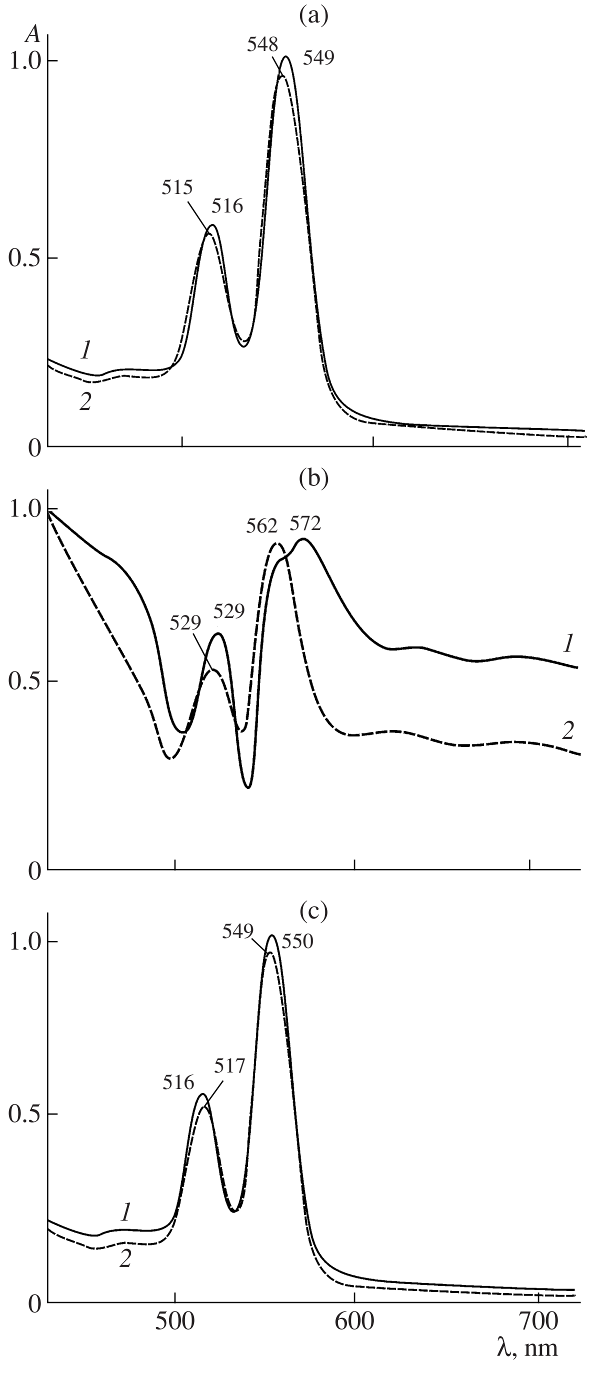


Fig. 2. Electronic absorption spectra of (*1*) PdMPOEP and (*2*) $Pd^{5,15}$DPOEP in (a) DMFA, (b) DMFA–H_2O–KOH–H_2O_2 mixture, and (c) $CHCl_3$; T = 298 K, c_{KOH} = 0.018 mol/l, and $c_{H_2O_2}$ = 3.61 mol/l.

tions in chloroform contained bands of initial PdP (Fig. 2c).

On the whole, the kinetics of transformations can be interpreted using the schemes of step elementary reactions presented below. Each of these steps corresponds to the chemical and structural principles substantiating overall equation (1) and kinetic equations (3) and (4),

$$PdP + H_2O_2 \xrightarrow{k_1} (H_2O_2)PdP, \text{ fast}; \tag{5}$$

$$(H_2O_2)PdP \xrightarrow{k_2} (O^{2-})PdP^{+\bullet} + H_2O, \text{ fast}; \tag{6}$$

$$H_2O_2 + OH^- \underset{k_{-3}}{\overset{k_3,\, K}{\rightleftarrows}} HO_2^- + H_2O; \tag{7}$$

$$(O^{2-})PdP^{+\bullet} + HO_2^- \xrightarrow{k_4} PdP + OH^- + O_2, \text{ slow} \tag{8}$$

and

$$PdP + H_2O_2 \overset{K_1}{\rightleftarrows} (H_2O_2)PdP; \tag{9}$$

$$(H_2O_2)PdP \xrightarrow{k_2'} (O^{2-})PdP^{+\bullet} + H_2O, \text{ fast}; \tag{10}$$

$$H_2O_2 + OH^- \overset{K_3}{\rightleftarrows} HO_2^- + H_2O; \tag{11}$$

$$(O^{2-})PdP^{+\bullet} + HO_2^- \overset{K_4}{\rightleftarrows} (HO_2^-)(O^{2-})PdP^{+\bullet}; \tag{12}$$

$$(HO_2^-)(O^{2-})PdP^{+\bullet} \xrightarrow{k_5'} PdP + OH^- + O_2, \text{ slow}. \tag{13}$$

The kinetic equations of limiting stages (8) and (13) are written as

$$\begin{aligned} -dc_{HO_2^-}/d\tau &= dc_{O_2}/d\tau = k_4 c_{(O^{2-})PdP^{+\bullet}} c_{HO_2^-} \\ &= k_4 K c_{PdP} c_{H_2O_2} c_{OH^-}, \end{aligned} \tag{14}$$

$$-dc_{(HO_2^-)(O^{2-})PdP^{+\bullet}}/d\tau = dc_{O_2}/d\tau = k_5' c_{(HO_2^-)(O^{2-})PdP^{+\bullet}}. \tag{15}$$

In (15),

$$c_{(HO_2^-)(O^{2-})PdP^{+\bullet}} = K_4 c_{(O^{2-})PdP^{+\bullet}} c_{HO_2^-}, \tag{16}$$

where $c_{HO_2^-} = K_3 c_{H_2O_2} c_{OH^-}$, $c_{(O^{2-})PdP^{+\bullet}} = c_{(H_2O_2)PdP}$, and $c_{(H_2O_2)PdP} = K_1 c_{PdP} c_{H_2O_2}$. Substituting $c_{HO_2^-}$ and $c_{(O^{2-})PdP^{+\bullet}}$ into (16) yields

$$c_{(HO_2^-)(O^{2-})PdP^{+\bullet}} = K_4 K_1 K_3 c_{PdP} (c_{H_2O_2})^2 c_{OH^-}. \tag{17}$$

Using (17) in (15) makes the equation for limiting stage (13) identical to experimental equation (4),

$$dc_{O_2}/d\tau = k_5 K_4 K_1 K_3 c_{PdP} (c_{H_2O_2})^2 c_{OH^-}. \tag{18}$$

Comparing Eqs. (14), (3) and (18), (4) and taking into account reaction heterogeneity, we find

$$k = k_4 K \tag{19}$$

and

$$k' = k_5 K_1 K_3 K_4. \tag{20}$$

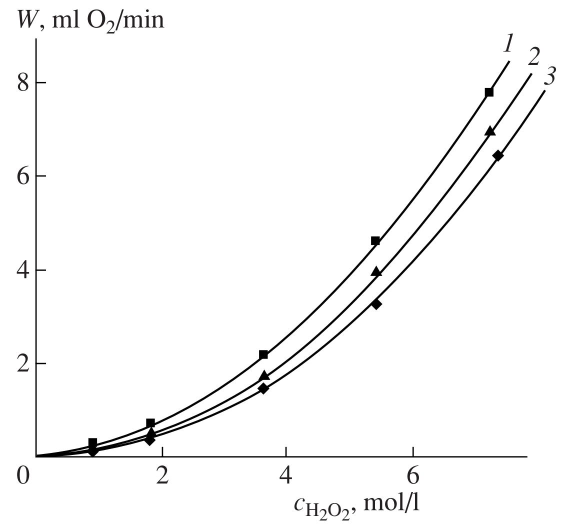


Fig. 3. Dependences of the rate of decomposition of H_2O_2 on its concentration in the presence of (*1*) PdOEP, (*2*) PdTetPOEP, and (*3*) $Pd^{5,10}$DPOEP; $c_{PdP} = 2.15 \times 10^{-5}$, 2.10×10^{-5}, and 2.90×10^{-5} mol/l, respectively; $c_{KOH} = 0.018$ mol/l; and $T = 343$ K.

Catalysis with PdP follows a more complex scheme than simple decomposition of H_2O_2 in an alkaline medium. At the initial stages (before the radical-ion mechanism begins to operate), we have a quasi-equilibrium system with acid–base catalysis [12],

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H^+, \quad (21)$$

$$2HO_2^- \longrightarrow 2OH^- + O_2. \quad (22)$$

According to [12], the rate of such a reaction increases up to the complete shift of equilibrium (21) to the right and then decreases. In experiments with PdP, the concentration of OH^- is much lower than $c_{H_2O_2}$ (Table 2), and the rate of the decomposition of H_2O_2 increases for all PdP as $c_{H_2O_2}$ grows; that is, all the experiments were performed in the region preceding maximum rate rise (Fig. 3). Within the first range of $c_{H_2O_2}$ concentrations, the PdP–H_2O_2–KOH system (Eqs. (5)–(8)) does indeed work as a quasi-equilibrium system [13], for which

$$c^0_{OH^-} = c_{OH^-} + c_{HO_2^-}. \quad (23)$$

Over the second range of $c_{H_2O_2}$ concentrations, one more equilibrium appears (Eq. (12)). Equation (14) can be solved with respect to k_4 and K by substituting c_{OH^-} from (23) and the equation for the K constant (Eq. (7)) into it,

$$c_{OH^-} = c^0_{OH^-}/(1 + Kc_{H_2O_2}). \quad (24)$$

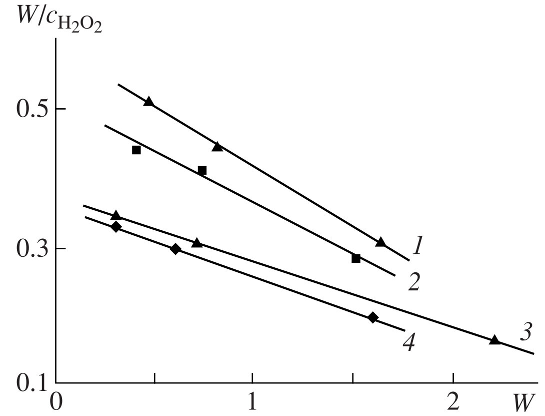


Fig. 4. Dependences of $W/c_{H_2O_2}$ on W in the presence of (*1*) PdTetPOEP, (*2*) $Pd^{5,10}$DPOEP, (*3*) PdOEP, and (*4*) PdMPOEP; $c_{PdP} = 2.10 \times 10^{-5}$, 2.90×10^{-5}, 2.15×10^{-5}, and 2.82×10^{-5}, respectively; $c_{KOH} = 0.018$ mol/l; and $T = 343$ K.

Equation (14) for the rate of the reaction can be written as

$$dc_{O_2}/d\tau = \frac{k_4 K c_{H_2O_2} c^0_{OH^-}}{1 + Kc_{H_2O_2}} = W, \quad (25)$$

taking into account that the PdP–H_2O_2–KOH system is heterogeneous. After transformations, we obtain an equation for a straight line in the coordinates $W/c_{H_2O_2}$–$f(W)$ (Fig. 4),

$$W/c_{H_2O_2} = k_4 K c^0_{OH^-} - KW. \quad (26)$$

The K and k_4 values were determined using dependence (26) (Table 4) and the experimental $c^0_{OH^-}$ = 0.018 mol/l value. The mean K value was 0.127 ± 0.04 l/mol. The K constant is larger than the constant of acid ionization of H_2O_2 in water (2.4×10^{-12} at 298 K [14]) by 11 orders of magnitude.

A comparison of the rate constants k for reaction (1) found experimentally with those calculated according to (26) (Kk_4, Eq. (19)) shows that they satisfactorily agree with each other and that k has a tendency to increase from PdOEP to PdTetPOEP.

We could expect a decrease in the rate of growth of W as $c_{H_2O_2}$ increases because of the transformation of all alkali present in a very low concentration into HO_2^- (Eq. (7)). Conversely, the experimental reaction order with respect to $c_{H_2O_2}$ increased from one to two in the second $c_{H_2O_2}$ range, which was related to the catalytic action of PdP. The decomposition of H_2O_2 then occurred in the first coordination sphere of the complex rather than in the solvent.

The validity of our conclusions and calculations finds support in the observation that the decomposition of hydrogen peroxide should indeed be first-order in H_2O_2 when the denominator in (25) can be set at 1 (that is, at low concentrations of H_2O_2).

The coordination of the second peroxide molecule (in the form of HO_2^-), which is a slow and irreversible reaction at low $c_{H_2O_2}$ concentrations (Eq. (8)), occurs rapidly to equilibrium state (12), and only then the product slowly decomposes with the regeneration of PdP and oxidation of HO_2^- in a two-electron redox process, which ends by releasing gaseous O_2 (Eq. (13)).

At standard temperature, PdOEP most strongly (by a factor of 14.4) increases the rate of the catalytic process (Table 3). The same complex decreases the activation energy most substantially, from 72 kJ/mol for the noncatalytic reaction to 40 kJ/mol in the presence of the metalloporphyrin (Table 3). The catalytic activity of the other complexes changes in the series

$$\underset{\xrightarrow{\text{Activation energy}}}{\overset{\xleftarrow{\text{Rate}}}{\text{PdOEP} > \text{PdMPOEP} \geqslant \text{Pd}^{5,\,15}\text{DPOEP} \geqslant \text{Pd}^{5,\,10}\text{DPOEP} \geqslant \text{PdTrPOEP} \geqslant \text{PdTetPOEP}}}.$$

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