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Influence of the Structure of the Macroheterocyclic Ligand on the Catalytic Properties of Metal Tetraarenoporphyrazine Complexes: I. Decomposition of Hydrogen Peroxide on Co and Fe Complexes

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Abstract—The catalytic activity of cobalt and iron complexes of the tetraarenoporphyrazine series in decomposition of hydrogen peroxide under heterogeneous conditions was studied. The catalytic properties of metal complexes are affected not only by the nature of the metal, but also by the peripheral structure of the macroheterocycle, varying in parallel with the electron-withdrawing power of the ligand.

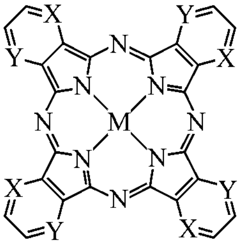
Metal complexes with macrocyclic ligands containing an extended closed π-conjugated system are being actively studied with the aim to develop effective catalysts and electrode materials. Among such complexes are, e.g., metal phthalocyanines.

The interest in the catalytic properties of these compounds steadily grows, but the main attention is focused on extending the range of catalytic reactions, varying the nature of the central metal ion, and introducing various substituents into the benzene rings of phthalocyanine, whereas studies concerning the effect of more cardinal modification of the ligand structure on the catalytic properties of the complexes are scarce.

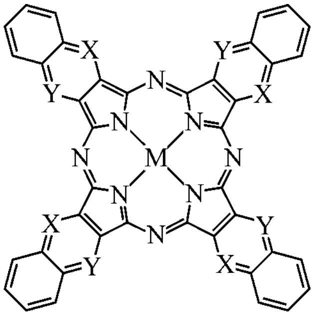
Our goal was to study how the periphery of the macroheterocyclic ligand affects the catalytic properties of metal tetraazaphorphine complexes in the test reaction of hydrogen peroxide decomposition under heterogeneous conditions.

The catalytic activity of iron phthalocyanine in hydrogen peroxide decomposition was discovered as early as 1938 [1]. However, the influence of the structure of the macroheterocyclic ligand on the catalytic function is still poorly understood.

As structural modification of the periphery of the tetraazaporphine ligand, we chose aza substitution in benzene fragments of phthalocyanine and their linear benzannelation. Thus, we studied the catalytic properties of cobalt and iron complexes of phthalocyanine (PcM) (**Ia**), tetra-2,3-pyridinoporphyrazine (2,3-PycM) (**IIa**), tetrapyrazinoporphyrazine (PzcM) (**IIIa**), 2,3-naphthalocyanine (2,3-NcM) (**Ib**), tetra-2,3-quinolinoporphyrazine (2,3-QlcM) (**IIb**), and tetra-2,3-quinoxalinoporphyrazine (2,3-QxcM) (**IIIb**).



Ia–IIIa



Ib–IIIb

X = Y = CH (**Ia**, **Ib**); X = CH, Y = N (**IIa**, **IIb**); X = Y = N (**IIIa**, **IIIb**).

Since these compounds are water-insoluble, their particle size is one of the major factors governing the catalytic performance. Therefore, all the samples of the metal complexes were prepared under similar conditions, which ensured approximately equal values of the microcrystal size and active surface area (Table 1).

In the course of the reaction, the solutions turned brown, which suggests that catalytic decomposition of hydrogen peroxide is accompanied by decomposition of the catalysts. A similar phenomenon was observed in [1, 2]. Therefore, the parameters of the catalytic reaction can be estimated fairly adequately only for

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Table 1. Specific surface areas of samples of metal phthalocyanines and related compounds

Metal complex	S_{sp}, $m^2 g^{-1}$	Metal complex	S_{sp}, $m^2 g^{-1}$
PcCo	14.2	2,3-NcCo	14.8
PcFe	12.5	2,3-QlcCo	13.7
2,3-PycCo	14.0	2,3-QlcFe	12.9
2,3-PycFe	12.7	2,3-QxcCo	12.9
PzcCo	15.4	2,3-QxcFe	12.7
PzcFe	13.6		

the initial reaction period; correspondingly, the catalytic performance of the metal complexes in decomposition of hydrogen peroxide, characterized by the apparent rate constants k_{app}, was evaluated from the initial portions of the kinetic curves; the error of k_{app} did not exceed 3%.

Decomposition of H_2O_2 under these conditions is described by the following equation:

$$-dC_{H_2O_2}/d\tau = k_v C^m_{H_2O_2} C^n_{cat}$$

or

$$-dC_{H_2O_2}/d\tau = k_{app} C^m_{H_2O_2},$$

$$k_{app} = k_v C^n_{cat},$$

where k_v is the true rate constant; $C_{H_2O_2}$, hydrogen peroxide concentration; C_{cat}, nominal molar concentration of the catalyst; n, reaction order with respect to the catalyst; and m, reaction order with respect to the substrate. Our experiments show that, under these conditions, the reaction is second-order with respect to the substrate and first-order with respect to the catalyst, which is consistent with published data for catalysis with metal phthalocyanines [3, 4]. This is due to the fact that the molecular crystal lattice of the catalysts is very loose and is permeable both for H_2O_2 molecules and for its decomposition products. As a result, each macroheterocycle molecule is operating, and fast diffusion processes exert no effect on the rate of the catalytic reaction. On the other hand, the specific surface areas of all the metal complexes are approximately equal (Table 1); hence, the concentration of the active centers on the surface of the heterogeneous catalyst is approximately equal and proportional to the nominal concentration of the catalyst.

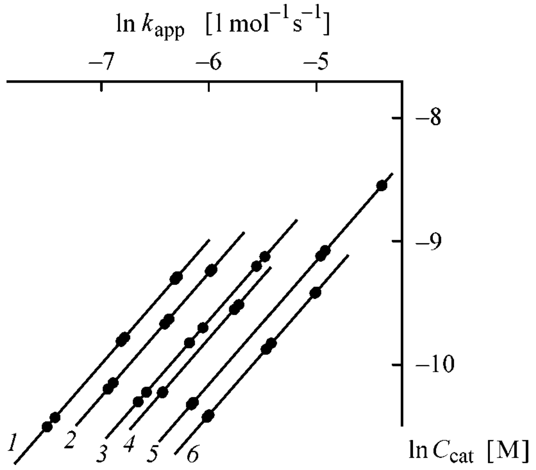

Fig. 1. Plot of $\ln k_{app}$ vs. $\ln C_{cat}$ for decomposition of H_2O_2 at 298 K in the presence of metal tetraarenoporphyrazine complexes: (*1*) 2,3-QxcCo, (*2*) 2,3-QlcCo, (*3*) PzcCo, (*4*) 2,3-PycCo, (*5*) PcCo, and (*6*) 2,3-NcCo.

Typical curves for determination of the reaction order with respect to the catalyst are shown in Fig. 1.

Since the reaction order with respect to the catalyst is the same for all the metal complexes **I** and **II**, the constant k_v determined from k_{app} and C_{cat} can be used both for comparing the catalytic activity of the compounds and for calculating the activation energy and entropy of the process.

The apparent rate constants calculated from the experimental data and the parameters C_{cat} and k_v are listed in Table 2. It is seen that, with all the ligands, the iron complexes are more active than their cobalt analogs. This fact is consistent with the previous data on the catalytic activity of the complexes of the same metals with other phthalocyanine derivatives [1, 5].

We also found that, with both metals, the rate of the catalytic reaction decreases in the order 2,3-QxcFe(Co) > 2,3-QlcFe(Co) > PzcFe(Co) > 2,3-PycFe(Co) > PcFe(Co) > 2,3-NcCo.

For the cobalt and iron tetraarenoporphyrazine complexes, we detected the compensation effect (Fig. 2) suggesting a common mechanism of hydrogen peroxide decomposition in all the cases, irrespective of the type of the macroheterocycle and nature of the metal.

It is of interest that introduction of electron-withdrawing substituents into the phthalocyanine molecule can both increase and decrease the catalytic activity of the metal complexes. On the contrary, aza substitution on the phthalocyanine periphery, which can be regarded as introduction of electron-withdrawing substituents into secondary conjugation circuits (as judged from variation of the spectroscopic and acid–base properties of the complexes [6–8]), enhances the activity of the catalysts.

Table 2. Kinetic parameters of decomposition of hydrogen peroxide, catalyzed with iron and cobalt tetraarenoporphyrazine complexes

T, K	$C_{cat} \times 10^4$, M	$k_{app} \times 10^5$, l mol^{-1} s^{-1}	$k_v \times 10^2$, l^2 mol^{-2} s^{-1}	$C_{cat} \times 10^4$, M	$k_{app} \times 10^5$, l mol^{-1} s^{-1}	$k_v \times 10^2$, l^2 mol^{-2} s^{-1}
		PcCo			PcFe	
298	21.10	3.29	1.56	24.56	4.91	2.00
	70.14	10.96	1.56	44.11	8.81	2.00
	123.64	19.32	1.56	66.21	13.23	2.00
303	20.32	4.53	2.23	25.09	7.09	2.83
	58.76	13.07	2.23	36.63	10.36	2.83
	95.72	21.18	2.22	56.17	15.89	2.83
313	12.17	5.44	4.47	18.58	10.14	5.46
	24.34	10.84	4.45	27.56	15.08	5.47
	53.94	24.05	4.46	38.65	21.14	5.47
		2,3-PycCo			2,3-PycFe	
298	16.08	3.63	2.26	16.95	4.51	2.66
	32.76	7.39	2.26	31.36	8.33	2.66
303	18.59	5.85	3.15	20.01	7.38	3.69
	36.24	11.42	3.15	37.83	13.95	3.69
313	12.08	7.20	5.96	24.97	17.15	6.86
	21.55	12.83	5.95	38.96	26.76	6.87
		PzcCo			PzcFe	
298	12.87	3.37	2.62	14.75	4.83	3.27
	23.49	6.13	2.61	22.73	7.43	3.27
	41.71	10.89	2.61			
303	13.56	4.86	3.59	15.27	6.82	4.47
	24.78	8.92	3.60	22.65	10.12	4.47
	47.49	17.08	2.61			
313	12.95	8.58	6.62	10.24	8.31	8.11
	27.46	18.18	6.62	15.01	12.14	8.09
		2,3-QlcCo			2,3-QlcFe	
298	9.73	3.74	3.84	8.71	4.11	4.71
	17.10	6.58	3.85	21.67	10.23	4.72
	25.54	9.82	3.85			
303	14.75	7.69	5.22	12.65	8.01	6.34
	19.35	10.11	5.22	28.08	17.77	6.33
	26.37	13.76	5.22			
313	3.13	2.92	9.35	9.92	11.01	11.10
	6.25	5.85	9.36	17.67	19.58	11.08
	15.75	14.75	9.37			
		2,3-QxcCo			2,3-QxcFe	
298	5.52	2.75	4.99	16.05	11.65	7.26
	11.03	5.49	4.98	27.87	20.22	7.26
	18.51	9.26	5.00			
303	3.92	2.60	6.64	10.70	10.22	9.55
	7.48	4.97	6.64	15.64	14.90	9.53
	12.93	8.56	6.62			
313	4.05	4.62	11.42	9.64	15.44	16.01
	6.87	7.84	11.41	16.34	26.19	16.03
	13.43	15.36	11.44			

Table 2. (Contd.)

T, K	$C_{cat} \times 10^4$, M	$k_{app} \times 10^5$, $l\ mol^{-1}\ s^{-1}$	$k_v \times 10^2$, $l^2\ mol^{-2}\ s^{-1}$
	2,3-NcCo		
298	24.42	2.97	1.22
	42.29	5.15	1.22
	67.10	8.18	1.22
303	23.12	4.09	1.77
	41.52	7.35	1.77
	65.16	11.53	1.77
313	12.37	4.46	3.61
	22.02	7.93	3.60
	41.39	14.89	3.60

The successive increase in the number of electron-withdrawing substituents on the periphery of the macroheterocyclic ligand enhances the catalytic activity of the metal complexes. For example, the rate constants increase by a factor of 2 in the series PcCo < 2,3-PycCo < PzcCo, PcFe < 2,3-PycFe < PzcFe, and 2,3-QlcFe < 2,3-QxcFe and by a factor of 4 in the series 2,3-NcCo < 2,3-QlcCo < 2,3-QxcCo. Thus, linear benzanellation appreciably enhances the activating effect of the aza atoms.

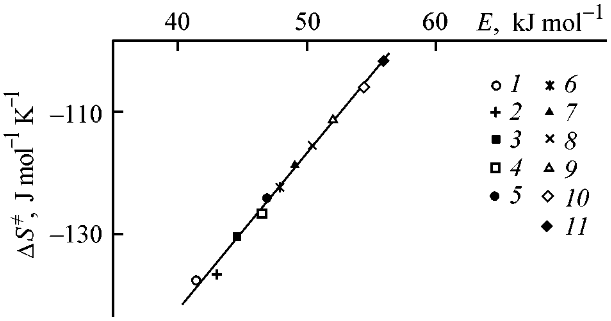

Fig. 2. Compensation effect in decomposition of H_2O_2 in the presence of metal tetraarenoporphyrazine complexes: (*1*) 2,3-QxcFe, (*2*) 2,3-QxcCo, (*3*) 2,3-QlcFe, (*4*) 2,3-QlcCo, (*5*) PzcFe, (*6*) PzcCo, (*7*) 2,3-PycFe, (*8*) 2,3-PycCo, (*9*) PcFe, (*10*) PcCo, and (*11*) 2,3-NcCo.

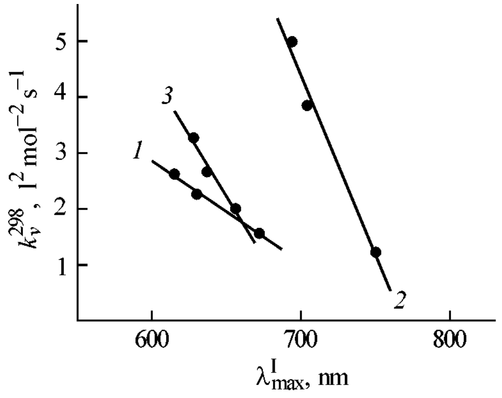

Fig. 3. Plot of k_v^{298} of H_2O_2 decomposition vs. λ^{I}_{max} of the complexes in DMSO: (*1*) PcCo, 2,3-PycCo, and PzcCo; (*2*) 2,3-NcCo, 2,3-QlcCo, and 2,3-QxcCo; and (*3*) PcFe, 2,3-PycFe, and PzcFe.

In contrast to aza substitution, benzannelation exerts a more complex effect on the catalytic activity of metal tetraarenophorphyrazines. For example, in going from PcCo to 2,3-NcCo, the rate constant decreases by 20%, whereas in the case of aza-substituted phthalocyanines it increases by a factor of 1.7 in going from 2,3-PycCo to 2,3-QlcCo and by a factor of 1.9 in going from PzcCo to 2,3-QxcCo. In iron complexes, the effect of benzannelation is still stronger.

According to modern views on the mechanism of catalytic decomposition of hydrogen peroxide on macroheterocyclic metal complexes, the process involves σ coordination of the peroxide anion with the central metal ion. The decrease in the electron density on the O–O bond due to extra coordination is the most important factor enhancing the oxidative power of the peroxide and allowing it to act as an oxidant toward another hydrogen peroxide molecule in the second stage [9].

Thus, an increase in the fractional positive charge on the central metal atom should enhance the catalytic activity. In this respect, our data on enhancement of the catalytic activity with increasing number of aza atoms on the molecular periphery seem to be quite logical. A decrease in the electron density in the main conjugation circuit and hence on the central metal ion, observed with increasing number of aza atoms and manifested in a regular hypsochromic shift of the first absorption band in the electronic spectra of tetraarenoporphyrazines, was already noted in optical studies of these compounds. The plot of k_v^{298} vs. λ^{I}_{max} for complexes **I** and **II** is approximately linear (Fig. 3).

Hence, catalysts of approximately equal activity can be obtained by combining a more active metal (Fe) with a less active ligand, and vice versa. For example, k_v^{298}(2,3-PycFe) ≈ k_v^{298}(PzcCo).

Thus, we found that the catalytic activity of iron and cobalt complexes of phthalocyanine analogs depends both on the nature of the central metal atom and on the structure of the macroheterocyclic ligand. These fragments interact in a complex fashion, which allows the process under consideration to be regarded as molecular catalysis, since the catalytic event involves the whole set of structural components of a metal tetraarenoporphyrazine.

EXPERIMENTAL

The catalytic properties of metal complexes were studied with a temperature-controlled rocker [10]. A reaction vessel was charged with 10 ml of 3% H_2O_2, after which an accurately weighed portion of a catalyst was added (the nominal concentration of the catalyst was varied from 0.5 to 12 mM). The variation of the substrate concentration was monitored by measuring the volume of the evolved oxygen. The initial concentration of hydrogen peroxide was determined by iodometric titration.

Experiments were performed in the temperature range 298–313 K at initial pH ~3.

Metal tetraarenoporphyrazine complexes were prepared and purified by published procedures [6–8] and identified spectroscopically. Before use, catalyst samples were washed until wash waters became neutral and sulfate-free. After that, the samples were dried to constant weight at 423 K and thoroughly ground.

The specific surface areas of the catalysts were determined by the BET procedure (low-temperature argon desorption).

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