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Kinetic Study of the Redox Properties of [5,10,15,20-Tetrakis(2,5-dimethoxyphenyl)porphyrinato]cobalt(II) in the Reaction with Hydrogen Peroxide

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Abstract—The reaction of [5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphyrinato]cobalt(II) with hydrogen peroxide in acetonitrile at 298 K has been studied by spectral methods. The kinetic parameters of the redox process have been determined, and a plausible mechanism has been proposed. The reaction involves generation of highly active cobalt porphyrin species capable of oxidizing hydrogen peroxide. Methoxy groups in the ligand have been found to act as redox activators to enhance the reactivity of the complex. The redox potentials of the complex determined by cyclic voltammetry indicate the possibility of formation of one-, two-, and three-electron oxidized species.

Keywords: cobalt porphyrin, hydrogen peroxide, redox reaction

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Important factors in the simulation of natural biocatalysts are structural similarity of the active centers of natural enzyme and its synthetic analogs and reproduction of high catalytic activity. Practical significance of metal porphyrins is determined by the broad spectrum of their structural features, which make it possible to use them in the design of biomimetics [1–8], including redox regulators of free radical oxidation, capable of preventing pathological changes that are accompanied by aging and heavy diseases.

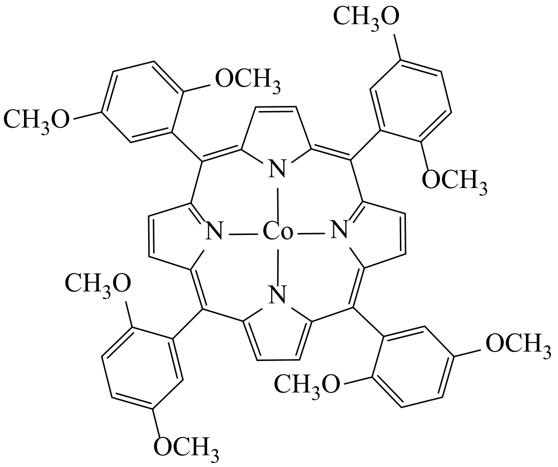
Active oxygen species initiate radical oxidation which leads to pathological changes and degradation of cells. The normal redox state and its stabilization are ensured by a complex enzyme system with redox regulators. However, there are situations such as intoxication where control over the level of generation of active oxygen species is disrupted. In these cases, additional administration of synthetic redox regulators with a good inactivating ability is necessary.

The activity and selectivity of metal porphyrins is determined by peripheral modification of the macrocyclic ligand and environment of the coordination center [9–17]. For instance, redox properties of cobalt porphyrins and dominant participation of the metal ion or macrocycle in redox reactions are related to the donor-acceptor properties of substituents and their number, as well as to the presence of alkyl ligands on the metal center [16, 17]. Cobalt porphyrins have been reported [12–15] to stimulate electrocatalytic reduction of oxygen according to the direct four-electron mechanism. It was noted that electrochemical behavior, catalytic activity, and selectivity of cobalt complexes are strongly influenced by the structure of their redox site. Depending on the nature and position of substituents on the macrocycle, cobalt porphyrins are capable of catalyzing reduction of oxygen via two- or or four-electron transfer. Cobalt porphyrins without substituents in the *meso* positions catalyze the reduction of oxygen to hydrogen peroxide and water [13]. *meso*-Phenyl-substituted cobalt porphyrins catalyze the reduction of oxygen to hydrogen peroxide, whereas those containing small alkyl groups in the *meso* positions may spontaneously form van der Waals dimers exhibiting a higher catalytic activity in the four-electron reduction of oxygen [13–15].

It is known that metal porphyrins are capable of decomposing peroxides [18–20]. However, there are problems concerning structure–activity relationships. Mechanisms of activation of free radical oxidation and ways of controlling it remain poorly studied. A solution to this problem may be modification of the macrocycle with peripheral redox-active substituents and variation of the environment of the coordination center to endow the complex with anti- or prooxidant properties.

Herein we report the results of studying the reaction of [5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphyrinato] cobalt(II) $Co^{II}TPP(OMe)_8$ with hydrogen peroxide in acetonitrile at 295 K. The effect of redox-active substituents on the catalytic activity of the complex has been demonstrated (Scheme 1).

Scheme 1.



$Co^{II}TPP(OCH_3)_8$

The reaction was carried out at a constant concentration of $Co^{II}TPP(OMe)_8$ (c = 5.49×10^{-6} M) and variable concentrations of hydrogen peroxide (6.34×10^{-6} to 2.56 M) at a constant temperature, and its progress was monitored by electronic absorption spectroscopy. Intermediate and final products were identified by UV and IR spectroscopy and mass spectrometry.

The reaction of $Co^{II}TPP(OMe)_8$ with hydrogen peroxide (c = 6.34×10^{-6}–1.29×10^{-4} M) was accompanied by variation of the electronic absorption spectra which showed two sets of spectral curves with isosbestic points. The first set of spectral curves displayed reduction in intensity and red shift of the band at λ 413 nm (Δλ = 19 nm), disappearance of the band at λ 528 nm and simultaneous appearance of a band at λ 544 nm (Fig. 1a, curves *1*, *2*). This pattern suggests one-electron oxidation of the complex at the metal cation ($Co^{II}\rightarrow Co^{III}$) [16, 21–24]. Change of the electronic structure of $Co^{II}TPP(OMe)_8$ during the reaction with ([H_2O_2] = 1.29×10^{-4} M, τ = 3 min) led to the appearance of a band at 547 cm^{-1} in the IR spectrum, which corresponds to Co–O vibrations. The ν(Co–N$_p$) band (456 cm^{-1}) shifted to lower frequencies by 12 cm^{-1}, which indicated displacement of the metal ion in the coordination center due to formation of the complex $(OH)Co^{III}TPP(OMe)_8$.

Transformation of the second set of spectral curves involved shift of the bands at λ 432 and 544 nm to 434 and 547 nm, respectively, with simultaneous appearance of new bands at λ 500 and 617 nm (Fig. 1a, curves *2*, *3*). These changes indicated oxidation of the porphyrin ligand in the complex [16, 22, 25–27] to form radical species $[Co^{III}TPP(OMe)_8^{\cdot}]^{2+}$. The IR spectrum of a mixture of $(OH)Co^{III}TPP(OMe)_8$ and hydrogen peroxide ([H_2O_2] = 1.29×10^{-4} M, τ = 10 min) showed a 7-cm^{-1} low-frequency shift of the ν(Co–O) band at 547 cm^{-1}

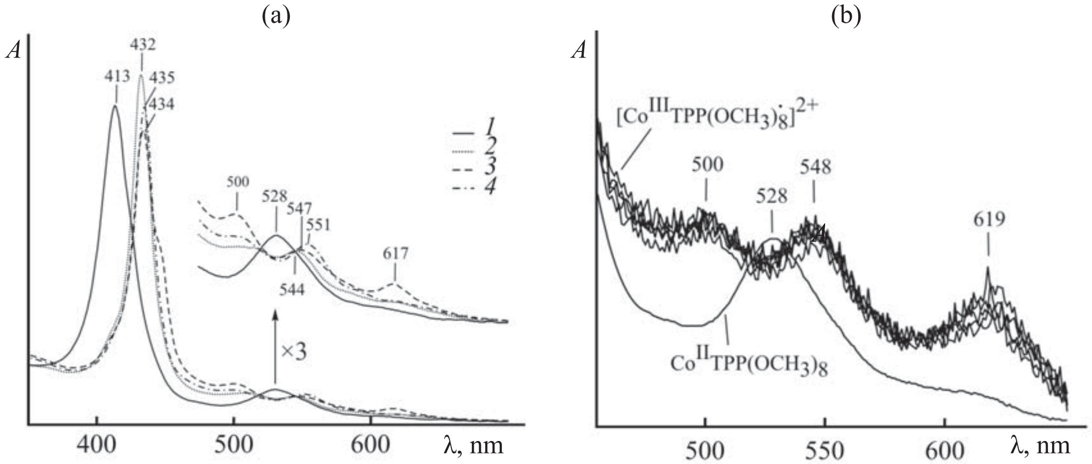


Fig. 1. Variation of the electronic absorption spectrum of $Co^{II}TPP(OMe)_8$ (c = 5.49×10^{-6} M) in the reaction with hydrogen peroxide (c = 1.29×10^{-4} M) in acetonitrile at 295 K. (a) [H_2O_2] = 1.29×10^{-4} M, (*1*) initial complex $Co^{II}TPP(OMe)_8$, (*2*) $[Co^{III}TPP(OMe)_8]^+$, (*3*) $[Co^{III}TPP(OCMe)_8^{\cdot}]^{2+}$, and (*4*) reduced form; (b) [H_2O_2] = 1.4 M.

and a 6-cm^{-1} high-frequency shift of the ν(Co–N$_p$) band at 444 cm^{-1}. No bands assignable to pyrrole C$_\alpha$–C$_\beta$ or C$_\alpha$–N bonds of the radical form with the unpaired electron localized on the porphyrin ring [19, 20, 27] were detected. Absorption bands at 619 (δ C–H in $OCH_2^{\cdot}$) [28] and 2867, 3160 cm^{-1} (ν C–H in $OCH_2^{\cdot}$) [29–31] were observed, which confirmed localization of the unpaired electron at the periphery of the macrocycle. In addition, an O–O band was present at 920 cm^{-1} [32]. The corresponding vibration frequency of hydrogen peroxide ranges from 880 to 830 cm^{-1} and is not observed at 1000–900 cm^{-1} [33], whereas O–O vibrations of MO_2 usually appear at 1152–990 cm^{-1} [34, 35]. Thus, the reaction mixture contained a compound other than hydrogen peroxide but possessing a peroxo group.

In the range of hydrogen peroxide concentrations from 8.0×10^{-4} to 1.29×10^{-2} M, the electronic absorption spectra showed only one set of curves with isosbestic points, which was attributed to the formation of $[Co^{III}TPP(OMe)_8^{\cdot}]^{2+}$. The electronic absorption spectrum of the latter is similar to curve *3* in Fig. 1a. The transformation of Co^{II} to Co^{III} is very fast.

Further raising hydrogen peroxide concentration ($[H_2O_2]$ = 1.14×10^{-1}–2.56 M) led to instantaneous two-electron oxidation of cobalt(II) porphyrin to the active form $[Co^{III}TPP(OMe)_8^{\cdot}]^{2+}$ (λ_{max} 434, 500, 548, 619 nm) capable of oxidizing hydrogen peroxide with evolution of oxygen. In the electronic absorption spectra we observed disruption of monotonicity of the spectral curve as a result of random discrete fluctuations with insignificant intensities (Fig. 1b). The IR spectrum of the reaction mixture, recorded 2 min after the addition of H_2O_2 to a concentration of 0.8 M, also showed ν C–H bands at 2882, 3178 cm^{-1} ($OCH_2^{\cdot}$), ν O–O band at 922 cm^{-1}, and a band at 1635 cm^{-1} which is typical of C=O stretching in quinones [36–38].

The mass spectrum of the reaction mixture with $[H_2O_2]$ = 1.29×10^{-1} M showed molecular ion peaks at *m*/*z* 868.7, 913.9, 929.8, 944.8, and 960.8, which were assigned to the ionic forms of the complexes $(OH)CoTPP(OMe)_4(O)_4$, $(OH)CoTPP(OMe)_7(O)$, $(OH)CoTPP(OMe)_7(OO)$, $(OH)CoTPP(OMe)_7(OCH_2OH)$, and $(OH)CoTPP(OMe)_7(OCH_2OOH)$, respectively. These species are intermediates and products of the reaction of $Co^{II}TPP(OMe)_8$ with hydrogen peroxide. Some of them could be highly active in further redox transformations. While initiating radical reactions, these species become labile and undergo unimolecular or induced decomposition.

At low hydrogen peroxide concentrations, the radical form of cobalt porphyrin is reduced with time The electronic absorption spectrum of the reduced form showed no band at λ_{max} 617 nm, and the other main bands decreased in intensity and shifted red by 1–4 nm relative to those of the active form (Fig. 1a; curves *3*, *4*). The observed shift may be related to both transformation of substituents in the phenyl rings and formation of dative bond with water or alcohol molecule. One of the oxidation products is cobalt(III) porphyrin with a benzoquinone fragment in the macrocycle, as followed from the IR and MS data (see above). The reduced complex cannot be detected spectrally at high hydrogen peroxide concentrations because of the high rate of formation of the radical form.

The oxidation of hydrogen peroxide is accompanied by decomposition of the complex, whose rate and degree depend on the concentration of H_2O_2. The degree of decomposition in 60 min is 3, 12, and 35% at low, medium, and high concentrations of hydrogen peroxide, respectively. The complex decomposes without change of the oxidation state of cobalt(III), as follows from the invariance of the position of the main bands in the electronic absorption spectrum (only their intensity decreases; Fig. 1b). The decomposition of the porphyrin chromophore is similar to the enzymatic degradation of heme and decomposition of chlorophyll [39–41]. It involves rupture of π–π conjugation system and cleavage of one methine bridge of the tetrapyrrole moiety at the α- or *meso* position to form a linear tetrapyrrole which then undergoes fragmentation to smaller molecules [42–44].

It should be noted that the reaction of unsubstituted cobalt tetraphenylporphyrin (CoTPP) with hydrogen peroxide ($[H_2O_2]$ = 1.5 M) is not accompanied by oxidation of the latter. The electronic absorption spectrum of the oxidized complex $[CoTPP^{\cdot}]^{2+}$ (λ_{max} 431, 498, 546, 616 nm) is similar to the spectrum of $[Co^{III}TPP(OMe)_8^{\cdot}]^{2+}$, which suggests similarity of the electronic structures of their molecules. However, the unpaired electron in $[CoTPP^{\cdot}]^{2+}$ is localized on the macrocycle, and this species is less active [45] than $[Co^{III}TPP(OMe)_8^{\cdot}]^{2+}$ where the unpaired electron is localized on the substituent.

The redox potentials of $Co^{II}TPP(OMe)_8$ were determined by cyclic voltammetry in acetonitrile. Its voltammogram showed three maxima in the region 0.22–1.25 V. The first half-wave potential, $E_{1/2}$ = 0.28 V,

Table 1. Kinetic parameters of the reaction of $Co^{II}TPP(OMe)_8$ with hydrogen peroxide in acetonitrile at 295 K

$c(H_2O_2)\times10^4$, M	$k_{ef}\times10^3$, s^{-1}
$[Co^{II}TPP(OMe)_8] = 5.49\times10^{-6}$ M	
0.063	4.064
0.129	7.831
1.290	30.22
$k_{v1} = 9.77$ s^{-1} mol^{-1} L^1	
0.129	0.182
1.290	0.448
8.000	0.807
12.900	1.192
40.000	1.539
$k_{v2} = 0.013$ s^{-1} mol^{-1} L^1	

corresponds to the oxidation of Co^{2+} to Co^{3+} [23]. The second and third potentials, $E_{1/2} = 0.62$ and 1.15 V, are related to the oxidation of porphyrin ligand, $L \leftrightarrow L^+$ and $L^+ \leftrightarrow L^{2+}$, respectively. The second potential is lower than that of $Co^{II}TPP$ ($E_{1/2} = 1.19$ V) where the unpaired electron is localized on the macrocycle [26]. These data indicate that the oxidation of peripheral methoxy substituent in $Co^{II}TPP(OMe)_8$ with the formation of $OCH_2^{\cdot}$ moiety is responsible for the more facile oxidation of that complex.

Taking into account the obtained spectral and electrochemical characteristics of $Co^{II}TPP(OMe)_8$, its two-electron oxidation with hydrogen peroxide can be described by Eq. (1). It should be noted that the oxidation of cobalt(II) therein is preceded by fast coordination of hydrogen peroxide molecule with its subsequent activation.

$$Co^{II}TPP(OCH_3)_8 + H_2O_2 \xrightarrow{k_{v1}} [Co^{III}TPP(OCH_3)_8]^+ \xrightarrow{k_{v2}} [Co^{III}TPP(OCH_3)_8^{\bullet}]^{2+}. \quad (1)$$

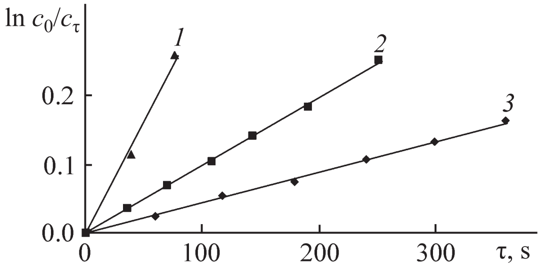


Fig. 2. Dependence $\ln(c_0/c_\tau)$–$f(\tau)$ for the first stage of the reaction of $Co^{II}TPP(OMe)_8$ with hydrogen peroxide. $[Co^{II}TPP(OMe)_8] = 5.49\times10^{-6}$ M, $[H_2O_2]$, M: (*1*) 1.2945×10^{-4}, (*2*) 1.29×10^{-5}, (*3*) 6.34×10^{-6}.

The linear plot of the concentration of the complex versus time [$\ln(c_0/c_\tau) = f(\tau)$] and satisfactory invariance of the effective rate constant k_{ef} (Fig. 2, Table 1) suggest first order of the reaction with respect to the cobalt complex. The rate constants of the direct reactions k_{v1} and k_{v2} ($k_{v2} << k_{v1}$, Table 1) and orders of the reaction in hydrogen peroxide ($n = 1$ and 0 for the first and second stages, respectively) were calculated from the linear dependence given by Eq. (2). On the basis of these kinetic parameters we derived Eqs. (3) and (4) for the rate of each stage of redox reaction (1).

$$\log k_{ef} = \log k_v + n \log c_{H_2O_2}, \quad (2)$$

$$-dc_{Co^{II}TPP(OCH_3)_8}/dt = k_{v1}\, c_{Co^{II}TPP(OCH_3)_8} \cdot c_{H_2O_2}, \quad (3)$$

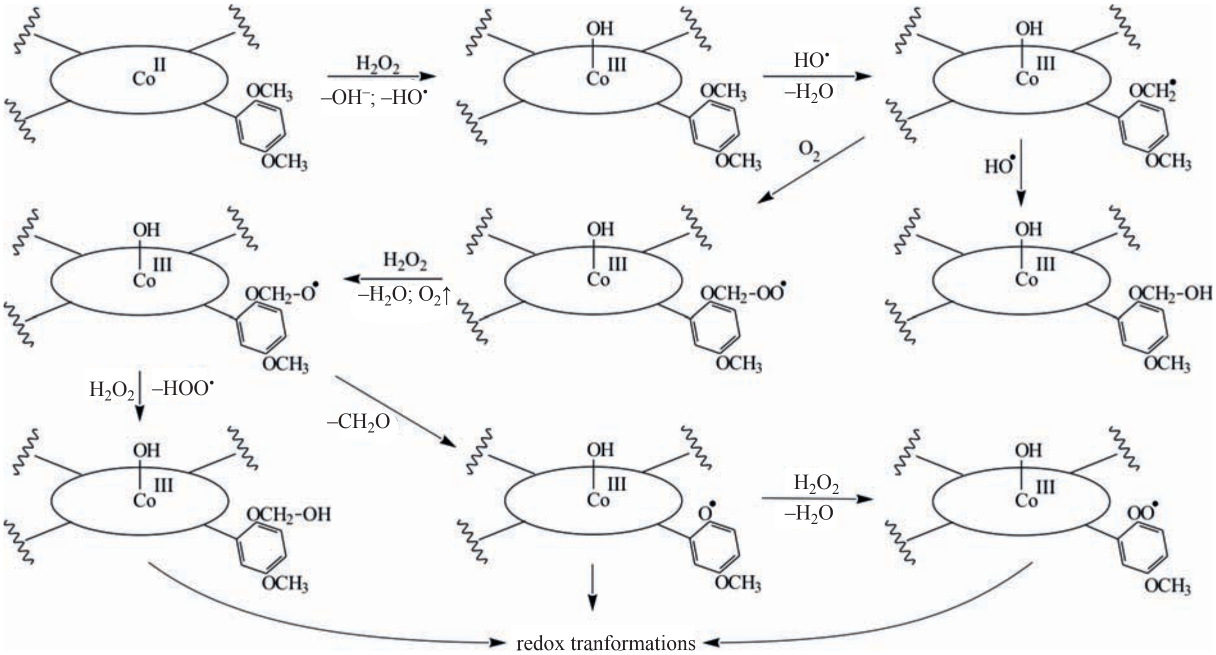
$$-dc_{[Co^{III}TPP(OCH_3)_8]^+}/dt = k_{v2} \cdot c_{[Co^{III}TPP(OCH_3)_8]^+}. \quad (4)$$

As noted above, the product of two-electron oxidation of $Co^{II}TPP(OMe)_8$ is the active form of cobalt(III) complex with the unpaired electron localized on the methoxy carbon atom. This radical adds oxygen molecule to give peroxide radical $OCH_2OO^{\cdot}$ [46] capable of oxidizing hydrogen peroxide to H_2O and O_2. This oxidation process can generate redox activators containing $OCH_2O^{\cdot}$, $ArOO^{\cdot}$, $ArO^{\cdot}$, and $Ar^{\cdot}$ moieties. Such intermediates, apart from oxidation of hydrogen peroxide, can be involved in other redox transformations leading to low-molecular-weight radical species and decomposition of the cobalt complex. In particular, there is the possibility of generation of peroxyl radical $HOO^{\cdot}$ which can also participate in radical reactions.

On the basis of spectral and kinetic data for the redox process we propose a plausible scheme for the formation of the active form of $Co^{II}TPP(OMe)_8$ and oxidation of hydrogen peroxide (Scheme 2). It should be kept in mind that the complete scheme includes a number of other redox reactions.

Our results led us to conclude that the active centers in the examined reaction of $Co^{II}TPP(OMe)_8$ with hydrogen peroxide are not only central metal ion and tetrapyrrole macrocycle but also peripheral substituents in the ligand. Localization of unpaired electron on the methoxy group and its further transformations give rise to a number of active intermediates that are also capable of oxidizing hydrogen peroxide to H_2O and O_2. Increase of the number of redox activators and their combination in a single molecule could make it possible to obtain new efficient synthetic analogs of natural oxidizing enzymes. The catalase activity of cobalt porphyrin induced by redox activators makes it a promising molecular system for the design of such models.

Scheme 2.



EXPERIMENTAL

The electronic absorption spectra were recorded in the range λ 350–800 nm at 295±0.1 K on a Varian Cary 50 spectrophotometer using 1-cm path length quartz cells. The mass spectra (MALDI-TOF) were obtained with a Shimadzu Axima Confidence mass spectrometer. The IR spectra were measured in the range 4000−390 cm^{-1} on a Bruker Vertex 80 spectrometer with Fourier transform, equipped with a Harrick MVP2 Series diamond ATR accessory (average scan number 64, resolution 2 cm^{-1}, room temperature, solvent acetonitrile). Electrochemical measurements were performed by cyclic voltammetry using an Elins P-30SM potentiostat according to the procedure described in [48]. Experiments were run in a three-electrode electrochemical cell at 25±0.5°C using freshly prepared solutions. The working electrode was a polished gold strip (Dropsens DRP-C220AT) firmly fixed on a Teflon cap; its active surface was thoroughly purified before each run first in distilled water and then in dimethylformamide. The working electrode was immersed in a cell containing a working solution, where its potential was stabilized within 10 min. Argon was bubbled through a capillary tube over 30 min to remove dissolved oxygen.

Acetonitrile was purified as described in [49]. Tetrabutylammonium perchlorate (98.0%, Aldrich) was purified by recrystallization from ethanol. A solution of the porphyrin complex [*c* = $(2–4)\times10^{-4}$ M] contained 0.02 M tetrabutylammonium perchlorate as supporting electrolyte. Hydrogen peroxide (30%) and acetonitrile (99.8%) were commercial products (Sigma–Aldrich).

[5,10,15,20-Tetrakis(2,5-dimethoxyphenyl)porphyrinato]cobalt(II) was synthesized as described in [47] by reaction of 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)-porphyrin (29.0 mg, 0.04 mmol) with cobalt(II) acetate tetrahydrate (47.0 mg, 0.19 mmol) in boiling acetonitrile for 60 min in an inert atmosphere. The reaction was assumed to be complete when the absorbance of the complex in the UV-Vis region of the electronic spectrum no longer changed. The solvent was evaporated under reduced pressure, and the precipitate was washed with water and purified by chromatography on aluminum oxide using chloroform as eluent. The product was dried under reduced pressure. Yield 95%. IR spectrum (MeCN), ν, cm^{-1}: 3041–2973 (C–H), 1653–1378, 1271–1263 (C_{arom}–O–C), 1168 (C–O, OCH_3), 1042 (C_{arom}–O–C), 729–655 (C–N), 457 (Co–N_p). Electronic absorption spectrum (MeCH), λ_{max}, nm (log ε): 413 (5.14), 528 (4.16). Mass spectrum (MALDI-TOF): *m*/*z*: 911.86 $[C_{52}H_{44}N_4O_8Co]^+$.

The kinetic parameters were determined according to [50]. The reaction was carried out at a constant concentration of $Co^{II}TPP(OMe)_8$ (*c* = 5.49×10^{-6} M) and different concentrations of hydrogen peroxide (*c* = 6.34×10^{-6}–2.56 M) in acetonitrile at 295 K. The electronic absorption spectra of a series of freshly prepared solutions were recorded at definite time intervals, and the optical densities at the absorption maxima of the complex were measured. The effective rate constants under excess hydrogen peroxide were calculated by formal first-order equation (5) with account taken of the change of optical densities at λ 413 and 434 nm.

$$k_{\mathrm{ef}} = 1/\tau \ln (c_0/c_\tau), \tag{5}$$

where c_0 and c_τ are the concentrations of the complex at the initial moment and time τ, respectively. The rate constant and order of the reaction with respect to hydrogen peroxide were determined by least-squares optimization of the dependence log k_{ef}–log $c_0(H_2O_2)$.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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