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COORDINATION COMPOUNDS

# Catalytic Activity of Octamethoxy-Substituted Cobalt(II) Tetraphenylporphyrinate in Tetraterpene Oxidation by Hydrogen Peroxide

**O. R. Simonova[a, *], S. A. Zdanovich[a], S. V. Zaitseva[a], and O. I. Koifman[a, b]**

[a] *Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia*
[b] *Ivanovo State University of Chemistry and Technology, Ivanovo, 153000 Russia*
**e-mail: ors@isc-ras.ru*

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**Abstract**—The catalytic activity of cobalt(II) porphyrinate in the oxidative degradation of β-carotene and lycopene by hydrogen peroxide is studied using spectroscopic methods. The kinetic parameters of the redox process are obtained, and its tentative mechanism is proposed. The catalytic activity is shown to depend on the composition of the coordination site and the presence of additional redox activators. Before oxidative degradation of tetraterpenes takes place, hydrogen peroxide gets coordinated to metal cation of the complex and is subsequently activated. The activation gives rise to a highly reactive intermediate that contains a radical on the methoxy moiety and can initiate free-radical oxidation.

**Keywords:** β-carotene, lycopene, oxidation, catalytic activity
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## INTRODUCTION

An imbalance in the pro- and antioxidant systems of the body disrupts the normal levels of reactive oxygen species (ROS) and free radicals, as well as causes their mutual conversions. This imbalance in oxidative metabolism activates lipid peroxidation followed by molecular damage to membranes and cell's genetic machinery. Therefore, severe diseases develop. In order to prevent or eliminate this process, ROS production needs to be eliminated. One of the methods for reducing hypersynthesis of ROS is to deliver synthetic analogs of intracellular enzymes and low-molecular-weight antioxidants inside the body.

Modeling of natural enzymes involves seeking and designing systems that exhibit high catalytic activity. Recent studies have shown that macrocyclic complexes of bioactive metals are successfully used as biomimetic catalysts [1–13]. Bharati et al. [12] showed that manganese porphyrinates exhibit high depolimerization and catalytic activities in the reactions of soft oxidation of organic aromatic pollutants. Zirconium(IV) *meso*-tetra(4-methoxyphenyl)porphyrin and its axial complexes with an electron-withdrawing ligand exhibit antioxidant properties and an antibacterial activity against Gram-positive and Gram-negative bacteria. Bajju et al. [13] reported that the high activity of zirconium complexes is caused by the fact that a single molecule contains two redox activators: a metal cation and a porphyrin ligand.

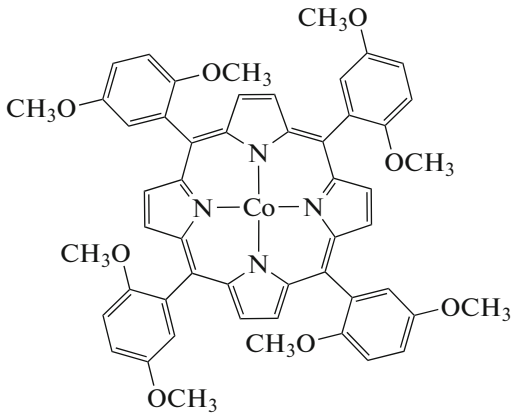
Due to the structural diversity of porphyrins and their analogs, these compounds have a broad range of properties, making it possible to control activity of a biomimetic system by increasing the reactive sites due to modification of the peripheral portion and the inner coordination sphere. Biomimetic studies using synthetic models of catalases and peroxidases based on these compounds show that a condition for exhibiting enzyme-like activity is as follows: highly covalent oxo complexes or high-reactivity intermediates carrying redox activators on their periphery are formed due to activation of the peroxide moiety and rupture of the O–O bond in it [14–23]. This encourages studies focused on the catalytic properties of macrocyclic tetrapyrrolic compounds and explains why cobalt(II) 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphinate was selected as a study object. Systematic studies on the effect of modifying the macrocyclic ligand structure and the environment of the active site of complexes on their catalytic properties in redox processes need to be conducted to get a detailed understanding how free-radical oxidation is activated.

It is known that the antioxidant system consists of enzymatic and non-enzymatic components. Carotenoids are the low-molecular-weight antioxidants that are involved in the second line of defense and remove excess bioradicals from the cell.

Carotenoids having a highly conjugated double-bond system are excellent targets for a free-radical

attack giving rise to complex intermediates [24–27]. On the one hand, these intermediates may exhibit low activity, but on the other hand they can participate in redox conversions, generate active radicals, and act as pro-oxidants. Oxidation of carotenoids is a complex process that has not been fully elucidated yet. Therefore, it is quite relevant to study the oxidative reactions involving carotenoids and test these compounds as potential antioxidants.

Oxidation of tetraterpenes (β-carotene and lycopene) by hydrogen peroxide ($H_2O_2$) in the presence of cobalt(II) porphyrinate in acetonitrile at 295 K was used in this study as a model for one of the stages of multi-component antioxidant defense.



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

## EXPERIMENTAL

**Cobalt(II) 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphinate ($CoTPP(OCH_3)_8$) (1)** was synthesized using the procedure described in [28]. 5,10,15,20-Tetrakis(2,5-dimethoxyphenyl)porphine (29.0 mg, 0.04 mmol) and cobalt(II) acetate $Co(AcO)_2 \cdot 4H_2O$ (47.0 mg, 0.19 mmol) were dissolved in acetonitrile and boiled in an inert gas atmosphere for 60 min. The reaction was considered complete when there were no more changes in the UV-visible region of the electronic absorption spectrum (UV—VIS spectrum) of the complex. After evaporating the solvent under vacuum and washing the precipitate with water, the complex was chromatographed on alumina (with chloroform used as an eluent) and vacuum-dried. The yield of cobalt(II) 5,10,15,20-tetrakis(2,5-dimethoxyphenyl)porphinate was 95%. UV–VIS spectrum of $Co(II)TPP(OCH_3)_8$ (acetonitrile ($\lambda_{max}$, nm (log ε)): 413 (5.14), 528 (4.16). The IR spectrum of $Co(II)TPP(OCH_3)_8$ (ATR, acetonitrile), $cm^{-1}$: 3041–2973 ν(C–H), 1653–1378 (vibrations of the porphyrin and benzene rings), 1271–1263 $\nu(C_{Ph}–O–C)$, 1168 ν(C–O, $–OCH_3$), 1042 $\nu(C_{Ph}–O–C)$, 729–655 ν(C–N), 457 $\nu(Co–N_p)$. MALDI-TOF: $m/z = 911.86$ for $[C_{52}H_{44}N_4O_8Co]^+$.

The UV–VIS spectra were recorded on a Varian Cary 50 spectrophotometer in the wavelength range of 350–800 nm at 295 K using quartz cells (optical path length 1 cm). The IR spectra were collected in the attenuated total reflection (ATR) mode on a Bruker Vertex V80 spectrometer equipped with a Harrick MVP2 SeriesTM accessory and a diamond prism in the frequency range of 4000–400 $cm^{-1}$ (the average number of scans collected = 64) with 2 $cm^{-1}$ resolution in acetonitrile at standard temperature.

The MALDI–TOF mass spectra were recorded on an Axima Confidence matrix-assisted laser desorption/ionization time-of-flight mass spectrometer.

The reagents used in this study were hydrogen peroxide (30%), acetonitrile (99.8%), carotene (97%), and lycopene (Ph. s. s.; Sigma-Aldrich).

The kinetic parameters of the reaction were obtained using the procedure described in [29]. The effective rate constants ($k_{eff}$) and the rate constants of carotene oxidation ($k_v$) at 295 K were determined with allowance for changes in absorbance ($A$) of the reaction mixture by optimizing the $\log(A_0 - A_\infty)/(A_\tau - A_\infty) - \tau$ and $\log k_{eff} - \log C^0_{tetraterp}$ dependences ($A_0$, $A_\tau$, and $A_\infty$ is the absorbance at operating wavelengths at $\lambda_{max}$ = 480 and 473 nm (for carotene and lycopene) at the initial instant and at the instant of reaction completion, respectively) at constant concentrations of the initial compound and hydrogen peroxide ($C_{H_2O_2}$ = 1.4 mol/L) and varied concentrations of carotene ($C_{car} = 2.3 \times 10^{-4}$–$5.9 \times 10^{-4}$ mol/L) and lycopene ($C_{lyc} = 4.9 \times 10^{-5}$–$1.35 \times 10^{-4}$ mol/L). The reaction order with respect to tetraterpene was determined from the slope ratio of the linear $\log k_{eff} - \log C^0_{tetraterp}$ dependence. The optimization was conducted using the least-squares method.

## RESULTS AND DISCUSSION

According to their mechanism of action, carotenoids are agents that quench reactive oxygen species and exhibit a preventive effect against a number of diseases caused by the lipid peroxidation of cell membranes and other free-radical processes occurring in the body. Lycopene is the most active carotenoid. The data regarding the effect of β-carotene on oxidation of biologically active substrates are rather controversial, since it was found to exhibit a pro-oxidative effect along with having an antioxidant activity. It is believed that the antioxidant and antiradical activities of β-carotene manifest themselves only at low oxygen partial pressures. Therefore, β-carotene oxidation by free radicals is being intensely studied both in aqueous media and in organic solvents. The time of oxidative degradation of β-carotene strongly depends on the nature of the oxidative agent and the medium [24, 30–32].

The catalytic activity of metal porphyrinates in oxidation of carotenoids by peroxides has been studied

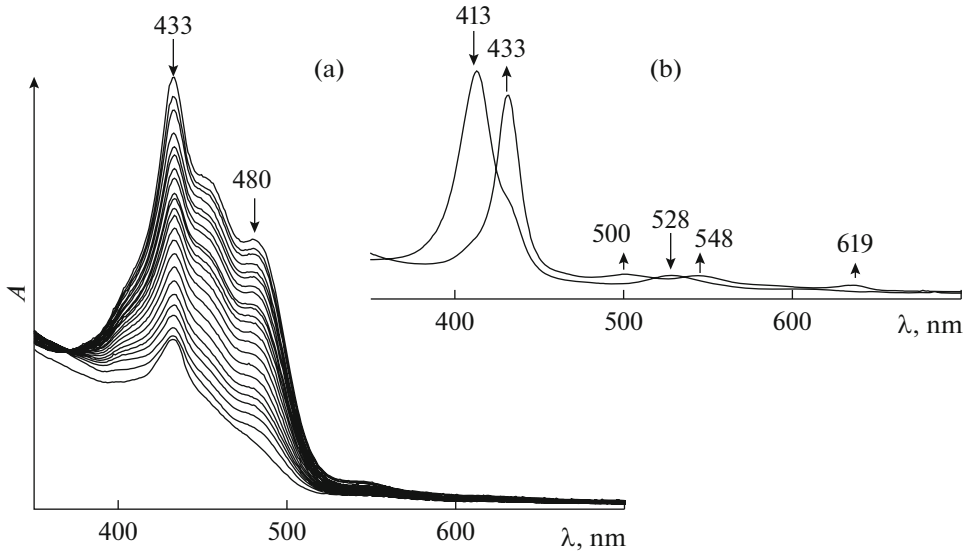



**Fig. 1.** (a) Changes in the UV–VIS spectra of carotene ($C_{car} = 4.86 \times 10^{-4}$ mol/L) in its reaction with hydrogen peroxide ($C_{H_2O_2}$ = 1.4 mol/L) in the presence of $Co^{II}TPP(OCH_3)_8$ ($C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L) in acetonitrile at 295 K; (b) changes in the UV–VIS spectra of $Co^{II}TPP(OCH_3)_8$ after its activation by hydrogen peroxide.

insufficiently and was discussed in a few works. The oxidative degradation of carotene by *tert*-butyl hydroperoxide in hexane and *meta*-chloroperoxybenzoic acid in benzene in the presence of ruthenium(II) and ruthenium(II) carbonyl(5,10,15,20-tetra-2,4,6-trimethylphenylporphyrin) used as co-oxidizing agents was studied in [19, 23, 25, 32]. It was found that the reactive oxo species of ruthenium porphyrinates O=Ru(IV) rarely participate in the reaction. It was shown [19, 23] that the oxo species $O{=}FeP^{+\bullet}{=}C{=}FeP$ (P = TAP or Pc) are reactive oxidative species in the (dimeric iron(IV) complex)–(*tert*-butyl hydroperoxide)–carotenoid system. Therefore, one should expect that the oxidized complex species that can be involved in tetraterpene degradation is formed when hydrogen peroxide is activated by cobalt(II) porphyrinate.

Addition of hydrogen peroxide ($C_{H_2O_2}$ = 1.4 mol/L) to an acetonitrile solution of cobalt(II) porphyrinate ($C_{CoTPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L) alters the UV–VIS of the complex. The bands at 413 and 528 nm are bathochromically shifted by 20 nm, while new bands simultaneously appear at 500 and 619 nm (Fig. 1). This transformation of the UV–VIS ($\lambda_{max}$ = 433, 500, 548, and 619 nm) indicates that a doubly oxidized complex species with the radical residing on the macrocycle was formed. The mechanism of formation of highly oxidized species of metal porphyrinates in a reaction with peroxides has been thoroughly described earlier [10, 19, 21–23, 27, 33–37]. It is worth mentioning that oxygen release in the reaction mixture is observed visually one minute later. In the UV–VIS spectra, this fact is manifested as loss of monotonicity by the spectral curve due to the emergence of low-intensity chaotic discrete fluctuations. IR spectroscopic and mass spectroscopic studies prove that a doubly oxidized species of cobalt complex was formed. After $H_2O_2$ ($C_{H_2O_2}$ = 1.0 mol/L) was added, the IR spectrum of the reaction mixture contains bands corresponding to the ν(C–H) vibrations in $-OCH_2^{\bullet}$ at 3178 and 2882 $cm^{-1}$ and a band at 1635 $cm^{-1}$ corresponding to the vibrations of C=O bonds in quinones [38, 39]. A ν(O–O) band is also observed at 922 $cm^{-1}$ [40]: this band is characteristic of a peroxy group residing outside hydrogen peroxide [41–43] (Fig. 2).

The mass spectrum of the reaction mixture ($C_{CoTPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 1.29 \times 10^{-1}$ mol/L) contains molecular ion peaks with $m/z$ = 913.9, 929.8, 944.8 and 960.8, which correspond to the ionic species of the $(OH)CoTPP(OCH_3)_7(O)$, $(OH)CoTPP(OCH_3)_7(OO)$, $(OH)CoTPP(OCH_3)_7(OCH_2OH)$, and $(OH)CoTPP(OCH_3)_7(OCH_2OOH)$ complexes (Fig. 3).

The resulting data demonstrate that activation of hydrogen peroxide gave rise to a doubly oxidized species containing a radical on the methoxy group $-OCH_2^{\bullet}$, which is rapidly converted to a $^{\bullet}OOR$ radical in the presence of atmospheric oxygen. These radicals are highly reactive and can oxidize hydrogen peroxide to $H_2O$ and $O_2$, which is actually observed during the reaction. The compounds detected by mass spectrometry (Fig. 3) are the intermediates and products of this redox process.

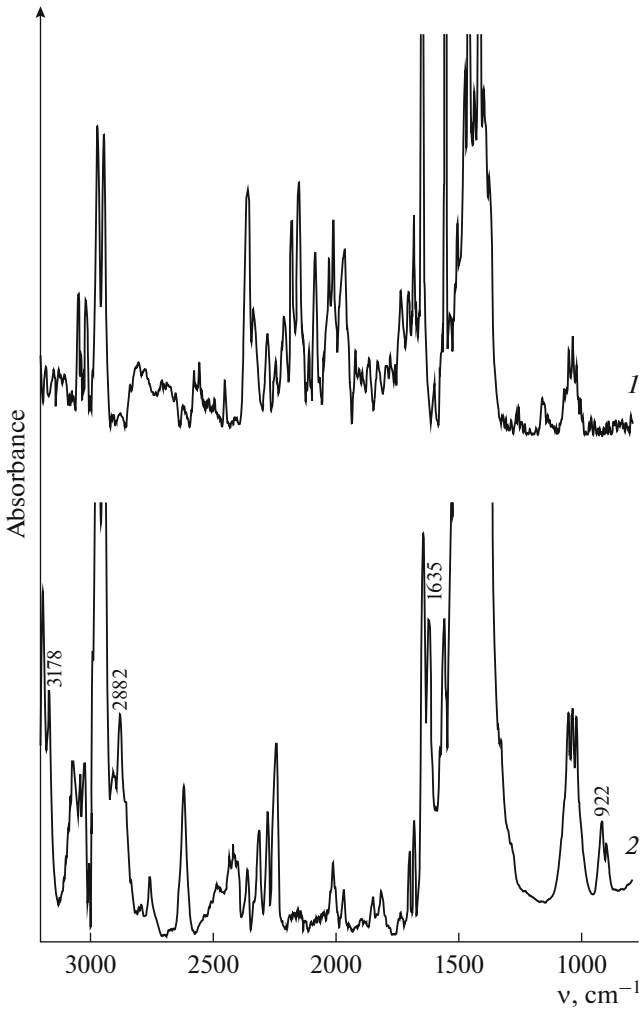



**Fig. 2.** IR spectra (acetonitrile) of (*1*) $Co^{II}TPP(OCH_3)_8$ and (*2*) the reaction mixture of $Co^{II}TPP(OCH_3)_8$ with $H_2O_2$ ($C_{Co^{II}TPP(OCH_3)_8} = 9.5 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 8 \times 10^{-1}$ mol/L).

A doubly oxidized cobalt(II) porphyrinate species is formed instantaneously under the discussed conditions. Therefore, a tetraterpene (carotene ($C_{car} = 2.3 \times 10^{-4}$–$5.9 \times 10^{-4}$ mol/L) or lycopene ($C_{lyc} = 4.9 \times 10^{-5}$–$1.35 \times 10^{-4}$ mol/L)) was added to the solution after this species had been detected in the UV–VIS spectra, and changes in absorbance of the mixture with time were recorded at 480 and 473 nm for carotene and lycopene, respectively (Fig. 1). The degree of tetraterpene degradation in the oxidation reaction is 98% during 2–4 h. In the absence of cobalt(II) porphyrinate, there were negligible changes in the UV–VIS spectra of the mixture; only 5% substrate degradation took place during 24 h.

It should be mentioned that carotene oxidization runs concurrently with oxidation of hydrogen peroxide. $O_2$ is released during the entire reaction. Meanwhile, when lycopene is added, oxygen release stops after 1–2 min.

Taking into account the spectral characteristics, oxidation of tetraterpenes by hydrogen peroxide in the presence of cobalt(II) porphyrinate is described by equation:

$$Co^{II}TPP(OCH_3)_8 + H_2O_2 \xrightarrow{k_{v1}} \left[Co^{III}TPP(OCH_3)_8^{\cdot}\right]^{2+} + \text{tetraterpene} \xrightarrow{k_{v2}} \text{oxidation products.} \quad (1)$$

The formally first-order effective reaction rate constants ($\log k_{eff}$) in the doubly oxidized cobalt(II) porphyrinate species–tetraterpene–acetonitrile system at constant complex concentrations correlate with $\log C_{tetraterp}$ (Fig. 4). The orders with respect to substrates ($n = 0$ for carotene and $n = 1$ for lycopene) were determined from the linear dependence of $\log k_{eff}$ on $\log C_{tetraterp}$ using Eq. (2) and the reaction rate constant (Table 1):

$$\log k_{eff} = \log k_v + n \log C_{tetraterp}. \quad (2)$$

The kinetic parameters obtained during the studies allow one to write down the reaction rate of tetraterpene oxidation as the following equations:

$$-dC_{car}/d\tau = kC_{\text{radical species}}, \quad (3)$$

$$-dC_{lyc}/d\tau = kC_{\text{radical species}}C_{lyc}. \quad (4)$$

The oxidative degradation of carotenoids is a complex and multistage process that gives rise to such intermediates as mono- and biradical species, apocarotenals, epoxides, apolycopenes, apolycopenals, etc., which eventually yield a number of low-molecular-weight products [24–27, 30–32, 44]. The zero reaction order with respect to carotene can be explained by the fact that the products of primary oxidation of the initial compound, but not the initial product itself, are involved in the rate-limiting step of the reaction. When studying this type of reactions in organic solvents in the presence of various oxidizing agents, de Jesus Benevides et al. [27] also found that the reaction was zero-order with respect to β-carotene.

An analysis of the kinetic data (Table 1) shows that lycopene oxidation occurs twenty times faster compared to carotene oxidation. This fact is consistent with the electrochemical studies of oxidation of natural carotenoids. Liu et al. [45] showed that the first and second oxidation potentials of lycopene are $E^0 = 0.50$ and 0.52 V; those for carotene are $E^0 = 0.54$ and 0.55 V, respectively.

It should also be borne in mind that reactive intermediates resulting from oxidation of hydrogen peroxide by the reactive cobalt(III) porphyrinate species carrying a radical on the methoxy group ($^{\cdot}OOR$) also

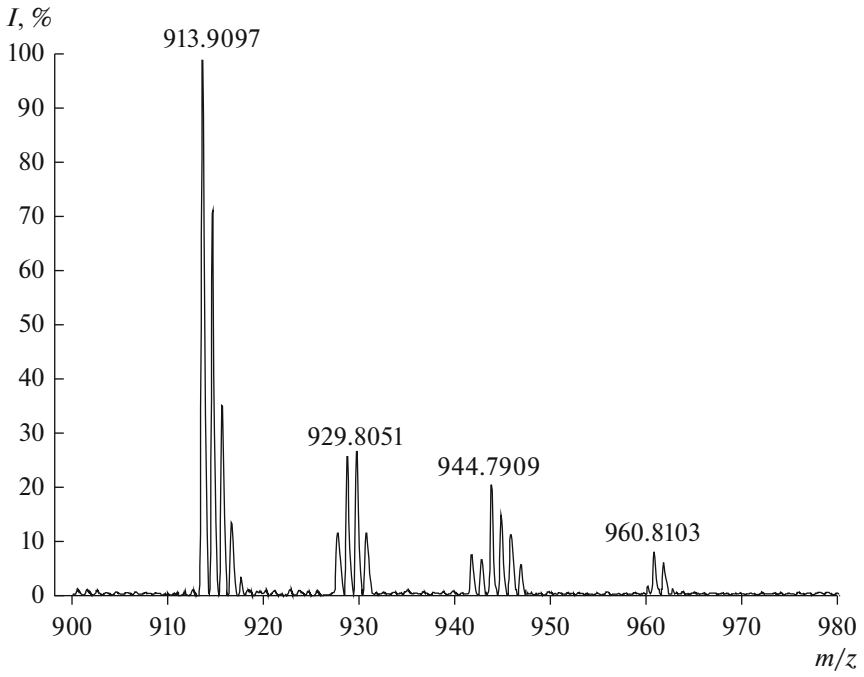



**Fig. 3.** Mass spectrum of the complex formed between $Co^{II}TPP(OCH_3)_8$ and $H_2O_2$.

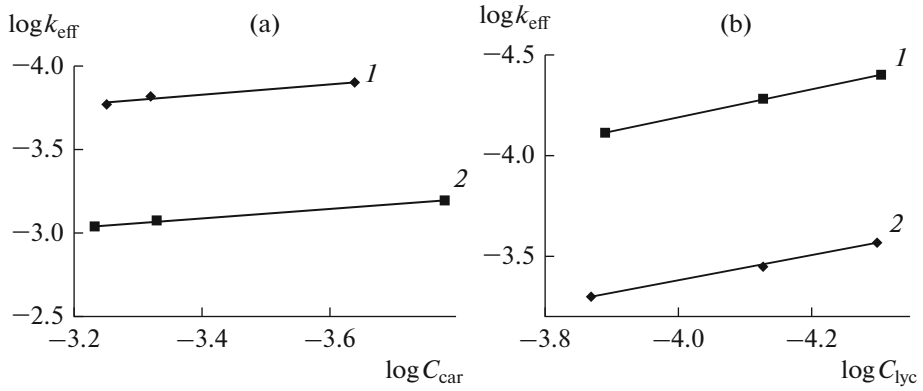



**Fig. 4.** $k_{eff}$ as a function of $C_{tetraterp}$ for the reaction of oxidation of tetraterpenes by hydrogen peroxide ($C_{H_2O_2}$ = 1.4 mol/L) in the presence of $Co^{II}TPP(OCH_3)_8$ ($C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L) (*1*) without imidazole and (*2*) with imidazole ($C_{Im} = 3.5 \times 10^{-3}$ mol/L) in acetonitrile at 295 K: (a) oxidation of carotene ($C_{car} = 1.67 \times 10^{-4}$–$5.87 \times 10^{-4}$ mol/L); (b) oxidation of lycopene ($C_{lyc} = 4.94 \times 10^{-5}$–$1.35 \times 10^{-4}$ mol/L).

make a certain contribution to the rate of oxidative degradation of β-carotene. This reaction proceeds concurrently, and the intermediates can be involved in substrate oxidation. While initiating free-radical reactions, these compounds become vulnerable and undergo monomolecular or induced degradation. Furthermore, Krieg biradicals [27], which can be involved in further oxidation both in a free form and being coordinated to a metal cation of the complex, may also act as reactive intermediates of the reaction. Therefore, the rate constant of carotene oxidation is an additive value. No concurrent reaction of hydrogen peroxide oxidation is observed during lycopene degradation. The reason for this is that lycopene rapidly neutralizes the ˙OOR radical located on the periphery of cobalt porphyrinate.

The oxidation of tetraterpenes accompanied by partial degradation of porphyrin chromophore of the complex is similar to enzymatic heme degradation and chlorophyll destruction [46, 47]. It is related to the disruption of π-conjugated system and rupture of a methine bridge in the tetrapyrrole ring at either α- or

**Table 1.** Kinetic parameters of tetraterpene oxidation by hydrogen peroxide in the presence of cobalt(II) porphyrinate in acetonitrile at 295 K

| $C_{car} \times 10^4$, mol/L | $k_{eff} \times 10^4$, $s^{-1}$ |
|---|---|
| $C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 1.40$ mol/L | |
| 2.31 | 1.26 |
| 4.80 | 1.53 |
| 5.63 | 1.70 |
| $k_v = 1.70 \times 10^{-3}\ s^{-1}\ mol^{-1}\ L^{-1}$ | |
| $C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 1.40$ mol/L, $C_{Im} = 3.5 \times 10^{-3}$ mol/L | |
| 1.67 | 6.39 |
| 4.69 | 8.48 |
| 5.87 | 9.10 |
| $k_v = 7.20 \times 10^{-3}\ s^{-1}\ mol^{-1}\ L^{-1}$ | |
| $C_{lyc} \times 10^5$, mol/L | $k_{eff} \times 10^5$, $s^{-1}$ |
| $C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 1.40$ mol/L | |
| 4.94 | 3.98 |
| 7.46 | 5.29 |
| 12.90 | 7.72 |
| $k_v = 3.70 \times 10^{-2}\ s^{-1}\ mol^{-1}\ L^{-1}$ | |
| $C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 1.40$ mol/L, $C_{Im} = 3.5 \times 10^{-3}$ mol/L | |
| 4.94 | 27.40 |
| 7.46 | 36.39 |
| 13.50 | 51.00 |
| $k_v = 1.32 \times 10^{-1}\ s^{-1}\ mol^{-1}\ L^{-1}$ | |
| $C_{Co^{II}TPP} = 6.8 \times 10^{-6}$ mol/L, $C_{H_2O_2} = 1.40$ mol/L | |
| 4.51 | 1.54 |
| 6.43 | 1.63 |
| 11.20 | 1.94 |
| $k_v = 1.65 \times 10^{-4}\ s^{-1}\ mol^{-1}\ L^{-1}$ | |

*meso* position as a radical or a low-molecular-weight radical moiety is located at this site. Therefore, a noncyclic tetrapyrrole is formed. It is further fragmented to low-molecular-weight compounds [48, 49]. The degree of degradation of cobalt porphyrinate during the oxidative degradation reaction is 10–15%. The final spectrum of the reaction mixture after tetraterpene oxidation corresponds to the doubly oxidized cobalt porphyrinate species $\left[Co^{III}TPP(OCH_3)_8^{\cdot}\right]^{2+}$. It was impossible to detect the reduced complex species because of the high rate of formation of the radical species.

The activity of the $\left[Co^{III}TPP(OCH_3)_8^{\cdot}\right]^{2+}$ species is proved by the fact that further degradation of tetraterpenes takes place without any hydrogen peroxide added. When the next portion of the substrate was added to the final solution, the bands corresponding to β-carotene and lycopene at 480 and 473 nm disappeared again, while the bands of the oxidized complex species were retained (their intensity being significantly decreased after five cycles). The rate constant of oxidative degradation of tetraterpenes remains virtually unchanged as demonstrated by the kinetic curves of the process (Fig. 5).

Axial ligands on a metal cation located in the *trans*-position with respect to the active site are known to be responsible for the activity of macrocyclic tetrapyrrolic compounds during binding and gas transport, electron transfer, and catalysis [4, 5, 8, 50–52]. Therefore, the effect of imidazole presence on the rate of oxidative destruction of tetraterpenes was studied. Imidazole incorporation (Im, $C_{Im} = 3.5 \times 10^{-3}$ mol/L) into the compound's coordination sphere is accompanied by formation of an electron donor–acceptor complex [53, 54]. Addition of hydrogen peroxide causes its oxidation and formation of a reactive species (UV–VIS, $\lambda_{max}$ = 433, 546 and 616 nm). The reaction rate of oxidative degradation of tetraterpenes involving this species increases several times (Table 1). However, after activation of hydrogen peroxide, the electron donor–acceptor complex forms a species that does not oxidize $H_2O_2$ to $H_2O$ and $O_2$. Stability of the reactive species was confirmed by the fact that the reaction of tetraterpene oxidation further proceeds at an almost identical rate without any hydrogen peroxide added (Fig. 5). It should also be mentioned that addition of imidazole stabilizes the complex, and its degradation is no more than 2% after five cycles of substrate oxidation. The nature of the reactive species of the liganded cobalt porphyrinate will be further investigated in a separate study.

In order to ascertain the relationship between catalytic activity and the presence of additional redox activators (namely, methoxy substituents), we studied the reaction of oxidative degradation of lycopene ($C_{lyc}$ = $4.5 \times 10^{-5}$–$1.12 \times 10^{-4}$ mol/L) by hydrogen peroxide ($C_{H_2O_2}$ = 1.4 mol/L) in the presence of the unsubstituted cobalt(II) tetraphenylporphyrinate (CoTPP, $C_{CoTPP} = 6.8 \times 10^{-6}$ mol/L). The UV–VIS spectrum of the oxidized $[CoTPP^{\cdot}]^{2+}$ complex ($\lambda_{max}$ = 431, 498, 546, and 616 nm) is similar to that of $\left[Co^{III}TPP(OCH_3)_8^{\cdot}\right]^{2+}$. This means that the molecules have the same electronic configuration. However, an electrochemical study showed that the second potential at which the porphyrin ligand is oxidized, $L \leftrightarrow L^+$ for CoTPP ($E_{1/2}$ = 1.19 V, the radical locates on the porphyrin ring [55]) is much higher than that for

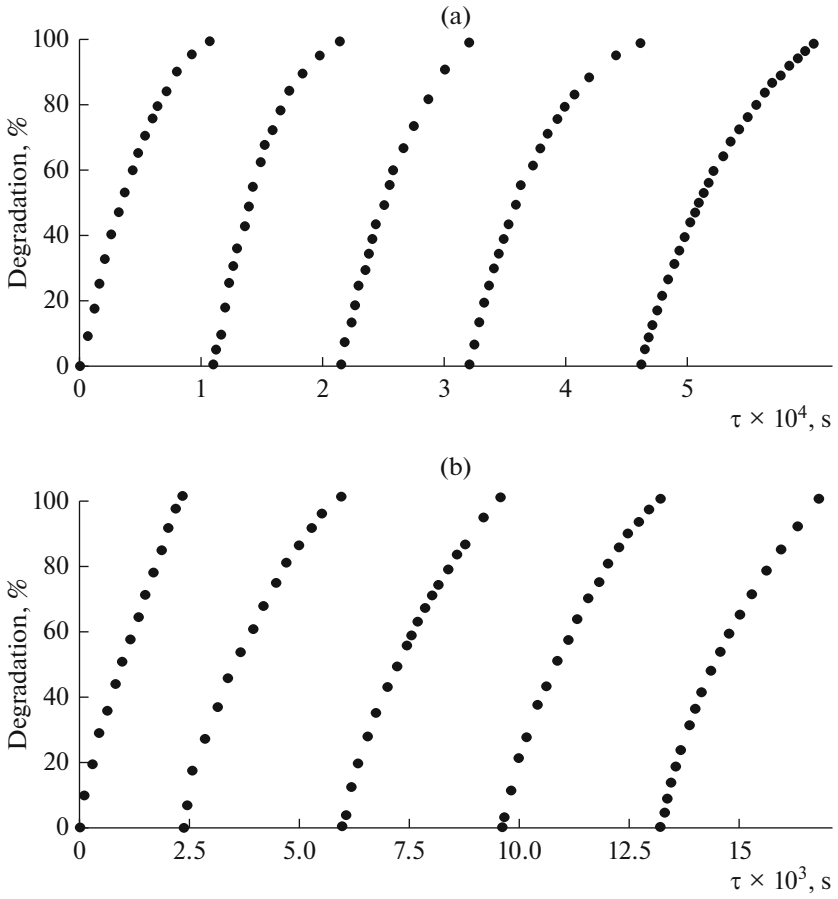



**Fig. 5.** Kinetics of oxidative degradation of lycopene ($C_{lyc} = 7.46 \times 10^{-5}$ mol/L) by hydrogen peroxide ($C_{H_2O_2} = 1.4$ mol/L) in the presence of $Co^{II}TPP(OCH_3)_8$ ($C_{Co^{II}TPP(OCH_3)_8} = 5.4 \times 10^{-6}$ mol/L), with the substrate being periodically added to the reaction mixture: (a) no imidazole added; (b) with imidazole added ($C_{Im} = 3.5 \times 10^{-3}$ mol/L).

$CoTPP(OCH_3)_8$ ($E_{1/2} = 0.62$ V, the radical locates on the $CH_3O$ moiety). These data suggest that the radical can be differently located within the macrocycle. The $[CoTPP^{\bullet}]^{2+}$ complex is not as reactive as $\left[Co^{III}TPP(OCH_3)_8^{\cdot}\right]^{2+}$ and does not oxidize hydrogen peroxide to $H_2O$ and $O_2$. The rate of lycopene oxidation in the presence of CoTPP is almost two orders of magnitude lower than that in the presence of $CoTPP(OCH_3)_8$ (Table 1). In this case, it is a zero-order reaction with respect to lycopene.

## CONCLUSIONS

The presence of methoxy groups acting as redox activators and variations in the coordination site composition due to inserting additional ligands considerably affect the catalytic activity of cobalt(II) porphyrinate in tetraterpene degradation. The high reactivity of the doubly oxidized radical cobalt porphyrinate species with respect to hydrogen peroxide and the reactive species of the liganded cobalt complex in oxidative destruction of tetraterpenes allows one to consider these compounds as promising catalysts of oxidation and as models of natural enzymes.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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