ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2018, Vol. 92, No. 11, pp. 2128–2134. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © O.R. Simonova, S.V. Zaitseva, E.Yu. Tyulyaeva, S.A. Zdanovich, O.I. Koifman, 2018, published in Zhurnal Fizicheskoi Khimii, 2018, Vol. 92, No. 11, pp. 1692–1699.

Kinetics of β-Carotene Oxidation in the Presence of Highly Active Forms of μ-Carbido Diiron(IV) Tetraphenylporphyrinate

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Received December 28, 2017

Abstract—The oxidative destruction of β-carotene in the presence of highly oxidized forms of μ-carbido-bis[(5,10,15,20-tetraphenyl-21H,23H-porphyrinato)iron(IV)] (**1** → **3**) or its analog with axially coordinated imidazole (**2** → **4**) obtained under the action of *tert*-butyl hydroperoxide ^{t}BuOOH was studied by spectrophotometry. It was found that compound **3** is the oxo form of compound **1** singly oxidized at the macrocyclic ligand (π radical cation) under the action of which β-carotene is oxidized with a rate constant $k = 3.3$ L^2 mol^{-2} s^{-1}. A conclusion is drawn that short-lived compound **4** has unique EAS and is capable of oxidizing ^{t}BuOOH to form O_2, which makes it possible to consider it the model of peroxidase. The value of *k* for the reaction with the participation of β-carotene and compound **4** ($k = 10.3$ L^2 mol^{-2} s^{-1}) is three times higher than that with the participation of compound **3**. If a new portion of β-carotene is added, the process of its oxidative destruction in the presence of compounds **3** or **4** occurs without additives of the dimeric complex and peroxide. A possible nature of compound **4** is discussed, as well as the influence of N-base in the coordination sphere of the complex on the nature of active intermediates and the rate of β-carotene decomposition.

Keywords: β-carotene, oxidation, iron(IV) μ-carbido-tetraphenylporphyrinate, kinetics, active intermediates, peroxidase model

DOI: 10.1134/S0036024418110390

INTRODUCTION

X-bridging (X = O, N, C) dimeric macrocyclic iron complexes are currently the subject of active studies as catalysts of redox reactions [1–8]. They are also biomimetics that model the composition and active centers of natural enzymes [9, 10] acting via oxygen atom transfer. These model complexes, by analogy with their monomeric analogs make it possible to study the reactivity of iron porphyrins and their chemical properties to understand complex structural and electron features of the active site. The peroxidase activity of iron-containing enzymes, which determines their ability to initiate metabolism and detoxication of peroxides by oxidation with the formation of O_2, is important for the antioxidant system of a human organism. The studies of mechanisms of such reactions, especially the nature of active intermediates, is complicated by their high reactivity and short lifetimes, which restricts the choice of experimental techniques applicable to the identification of intermediate oxidized forms. The key intermediates in chemical transformations of substrates under the action of enzymes are the highly oxidized form of porphyrinoid complexes O=Fe(IV) and the π radical cation form oxidized at the macrocyclic ligand [11–13]. However, the question of the nature of oxidizing active species remains open [14–17]. In its turn, β-carotene, which is a natural dye with various biological functions having a highly conjugated system of double bonds is a perfect subject of free radical attack in oxidation with complex reaction products [18–22].

The goal of this work was to study the reactivity and fundamental features of oxidants in heme-containing enzymes using μ-carbido diiron(IV) complex with 5,10,15,20-tetraphenyl-21H,23H-porphyrin as a model compound when its forms participate in the oxidative decomposition of β-carotene.

EXPERIMENTAL

μ-Carbido-bis[(5,10,15,20-tetraphenyl-21H,23H-porphyrinato)iron(IV)] $[FeTPP]_2C$ (1) was synthesized according to the technique described in [23] from ClFeTPP obtained and isolated according to reference data [24]. 100 mg (0.14 mmol) of ClFeTPP were dissolved in 20 mL of isopropanol. KOH (1 g, 0.018 mmol) was added, and the mixture was boiled at 120°C for 20 min with stirring. The reaction was accompanied by changes in the color of the solution from red wine to magenta. $CHCl_3$ (5 mL) was added to the reaction mixture dropwise, and then the reaction mixture was cooled to 40°C and diluted with water. The organic layer containing [FeTPP]$_2$C was separated and chromatographed on Al_2O_3 (Brockmann activity II) using CH_2Cl_2 as an eluent. EAS in C_6H_6 (λ_{max}, nm): 400, 522. IR spectrum: (C_6H_6, ν, cm^{-1}), 960 (ν_{as} Fe=C=Fe), 423 (ν_s Fe=C=Fe), 461 (Fe–N$_{TPP}$). ESI–MS: m/z [FeTPP]$_2$C]$^+$ 1349.3. For $C_{89}H_{56}N_8Fe_2$ calculated 1349.17.

μ-Carbido-bis[(imidazole)(5,10,15,20-tetraphenyl-21H,23H-porphyrinato)iron(IV)](Im)$_2$[FeTPP]$_2$C (2). Imidazole ($C_{Im} = 10^{-3}$ mol/L) was added to a solution of [FeTPP]$_2$C ($C_1 = 10^{-6}$ mol/L) in benzene. The reaction of formation of bis-axial complex was controlled by changes in EAS of the reaction mixture. EAS in C_6H_6 (λ_{max}, nm): 403, 526, 562, 605. IR spectrum (C_6H_6, ν, cm^{-1}): 936 (ν_{as} Fe=C=Fe), 419 (ν_s Fe=C=Fe), 435 (Fe–N$_{TPP}$), 478 (Fe–N$_{Im}$). ESI-MS: m/z [(Im)$_2$[FeTPP]$_2$C]$^+$ 1485.1. For $C_{95}H_{64}N_{12}Fe_2$ calculated 1485.33.

Oxidized [FeTPP]$_2$C (3) and (Im)$_2$[FeTPP]$_2$C (4) were obtained by the reaction of compounds **1** and **2**, respectively, with ^{t}BuOOH ($C_{^t\mathrm{BuOOH}} = 2.3 \times 10^{-4}$–$2.3 \times 10^{-3}$ mol/L) in benzene. The reactions of formation of oxidized forms of complexes were controlled by changes in EAS of the reaction mixture.

EAS (**3**) in C_6H_6 (λ_{max}, nm): 413, 572, 627.

IR spectrum (C_6H_6, ν, cm^{-1}): 1295 (C_α–C_β, C_α–N), 914 (ν_{as} Fe=C=Fe), 422 (ν_s Fe=C=Fe), 435 (Fe–N$_{TPP}$).

EAS (**4**) in C_6H_6 (λ_{max}, nm): 414, 569, 609.

EAS spectra were recorded using a Cary 50 instrument. IR spectra were obtained by the attenuated total reflection method using Bruker Vertex V80 spectrometer in the range of frequencies 4000–400 cm^{-1} (on the average 64 scans) with a resolution of 2 cm^{-1} at a standard temperature. IR spectra were recorded using an MVP 2 SeriesTM (Harrick) attachment with a diamond crystal. The products of oxidative destruction were analyzed by electrospray ionization mass spectrometry using a Bruker microTOF spectrometer.

We used *tert*-butyl hydroperoxide ^{t}BuOOH (98%) and carotene (97%) from Sigma-Aldrich and dried benzene.

The apparent rate constants k_{app} and the rate constants k of carotene oxidation at 298 K were determined by changes in absorbance (A) of the reaction mixture at a working wavelength that corresponded to the maximum of carotene absorption band λ_{max} = 463 nm at constant concentrations of initial compounds **1**, **2**, and ^{t}BuOOH and different concentrations of carotene by least-squares optimization of the dependence $\log(A_0 - A_\infty)/(A_\tau - A_\infty)$–$\tau$ and $\log k_{app}$ – $\log C^0_{Car}$ (A_0, A_τ, and A_∞ are absorbances at a working wavelength at the initial, current and final moment of time, respectively).

DISCUSSION

The structural diversity of carotenoids belonging to one of the most important groups of natural dyes enables their diverse functions. To be specific, the antioxidant properties of β-carotene, which has a polyene structure are stipulated by its ability to enter oxidation reactions under the action of free radicals. Reactions of this type in the aqueous medium and organic solvents are actively studied. Depending on the nature of oxidant and reactivity, the time required for β-carotene oxidative destruction reaction differs [18, 20, 25, 26]. The catalytic role of metalloporphyrins in β-carotene oxidation was considered in very few publications: (tetrakis(dichlorophenyl)porphyrin) ruthenium(II) and (5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porhyrin)ruthenium(II) carbonyl were chosen as co-oxidants in carotene oxidative destruction with ^{t}BuOOH in hexane [27] and meta-chloroperoxybenzoic acid in benzene [19], respectively. It was noted in the cited works that ruthenium porphyrin complexes enter the reaction in the active oxo form O=Ru(IV), but the mechanism of activation for these species has not been proposed. In connection with the above-mentioned catalytic activity of μ-dimeric iron porphyrinoid complexes, the reaction between β-carotene and oxidized derivatives of compound **1** or its analog **2** with axially coordinated imidazole was carried out.

The initial EAS (Fig. 1, line *1*) of compound **1** in benzene ($C_1 = 10^{-6}$ mol/L) changed upon adding ^{t}BuOOH ($C_{^t\mathrm{BuOOH}} = 2.3 \times 10^{-3}$ mol/L) and transformed to the spectrum of compound **3**, which is singly oxidized π radical cation of the oxo form of the initial complex O=FeTPP$^{+\bullet}$=C=FeTPP. The mechanism of formation of highly oxidized forms of μ-dimeric tetrapyrrole iron complexes, which were reliably identified by various physicochemical methods, under the action of H_2O_2 and organic peroxides is well known [1–8, 28, 29]. Therefore, the bathochromic shift of the B band from 400 to 413 nm and the growth of Q bands at 570–630 nm in the EAS were attributed to the formation of π radical cation **3** (Fig. 1, line *2*). A change in the electron structure of the dimeric iron complex is reflected in the appearance of the absorption band in the IR spectrum at 1290 cm^{-1}, which is related to the vibrations of the C_α–C_β and C_α–N bonds in pyrrole rings (Fig. 2a) [30]. When changes in the EAS ceased, β-carotene (C_{Car} = (4.33–8.54) × 10^{-4} mol/L) was added to the solution, and changes in the absorbance were recorded at a wavelength equal to the maximum of the carotene absorption band λ_{max} = 463 nm (Fig. 1, lines *3*, *4*) until its complete disappear-

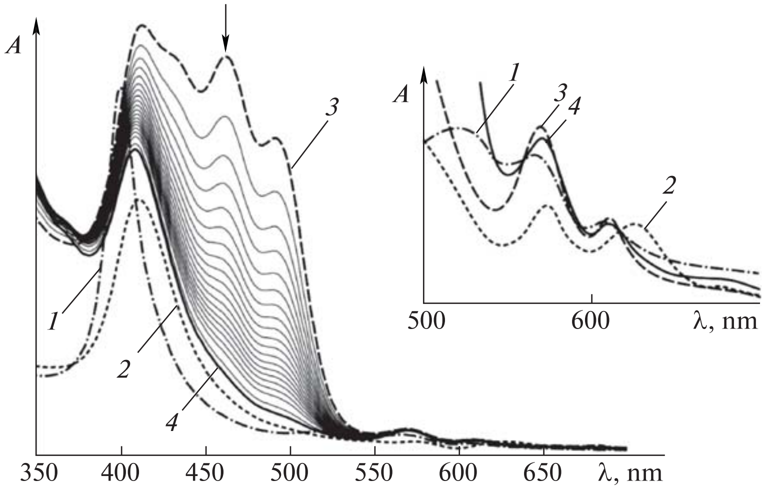


Fig. 1. Electron absorption spectra of compounds in benzene: (*1*) compound **1** ($C_1 = 10^{-6}$ mol/L); (*2*) compound **3** ($C_{^t\mathrm{BuOOH}} = 2.3 \times 10^{-3}$ mol/L); (*3*) compound **3** after adding β-carotene ($C_{\mathrm{Car}} = 4.3 \times 10^{-4}$ mol/L); (*4*) the same as *3* upon reaction completion.

ance. Note that EAS of β-carotene remains unchanged in pure benzene, and in the presence of ^{t}BuOOH for 6 h the intensity of absorption bands only slightly decreases. If compound **3** participates, the decomposition of β-carotene occurs for several minutes. The apparent rate constants of the reaction are of the formal first order ($\log k_{\mathrm{app}}$) in the **3**–β-carotene–benzene system at a constant concentration of metalloporphyrin linearly correlate with $\log C_{\mathrm{Car}}$ (the correlation equation is $\log k_{\mathrm{app}} = 0.501 + 0.931\log C_{\mathrm{Car}}$, $R^2 = 0.994$). The value of $\tan \alpha \approx 1$ corresponds to the first order with respect to substrate and, therefore, to the second-order rate equation (1) with a reaction rate constant $k = 3.3$ L^2 mol^{-2} s^{-1}.

$$-dC_{\mathrm{Car}}/d\tau = kC_3C_{\mathrm{Car}}. \qquad (1)$$

The oxidative decomposition of β-carotene is a complex multiple-step process that occurs via the formation of intermediate mono- and biradical forms, apocarotenals, epoxides and other species and that leads to the formation of many products (>15) [18–20, 25–27]. The reactions of this sort were studied earlier in the mixture of organic solvents. Under the action of various oxidants, the zeroth order with respect to β-carotene (see [20] and references therein) was found. It can be explained by the participation of the products of primary oxidation of the initial compound rather than the initial compound itself in the rate-limiting step. However, when studying analogous reactions in food products, like in our case, the order with respect to β-carotene was the first [20].

The final spectrum of the reaction mixture after the disappearance of the band corresponding to β-carotene does not coincide with the spectrum of any of the initial compounds. Nor does it coincide with the spectra of the initial compound **1** or its π radical cation form **3**. This intermediate (compound **5**) is likely the result of hemolytic O–O bond cleavage in the peroxide $-\mathrm{O}^\bullet$ coordinated to the iron cation, which then transforms into the radical cation on the macrocycle, and the product of further reduction in the process of β-carotene oxidation (Scheme 1).

Moreover, Criegee biradicals can be intermediates in the reaction [20], which are capable of participating in further oxidation both in the free form and coordinated on iron cation in the dimeric complex. The presence of active species in the solution is supported by further reaction of carotene decomposition without ^{t}BuOOH additives. When adding a new portion of the substrate to the final mixture, the β-carotene band, which appeared at 463 nm, disappears again, while the bands of oxidized form **5** are retained. Their intensity does not change upon ten cycles. The rate constant of the process remains almost unchanged during these ten cycles. Figure 3a shows the kinetic curves of the oxidative decomposition of β-carotene in the presence of compound **3** if the substrate is periodically added to the reaction mixture. Table 1 shows the reaction products identified by the ESI–MS method using reference data.

The action of compound **3** in the reaction studied is analogous to the action of the π radical cation of natural enzymes (compound I) participating in oxidation reactions in living organisms and various biomimetics (Scheme 1).

It is well known that axial ligands on iron cations that are in the trans position to the active site determine the activity of these compounds when binding and transporting gases, in electron transfer, and in catalysis [23, 28, 31–35]. To elucidate the effect of

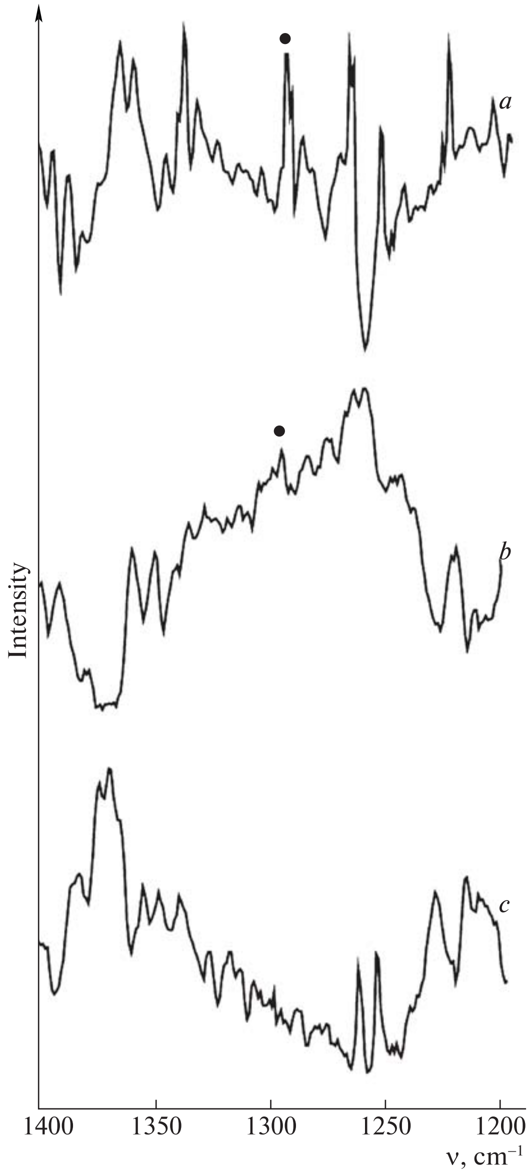
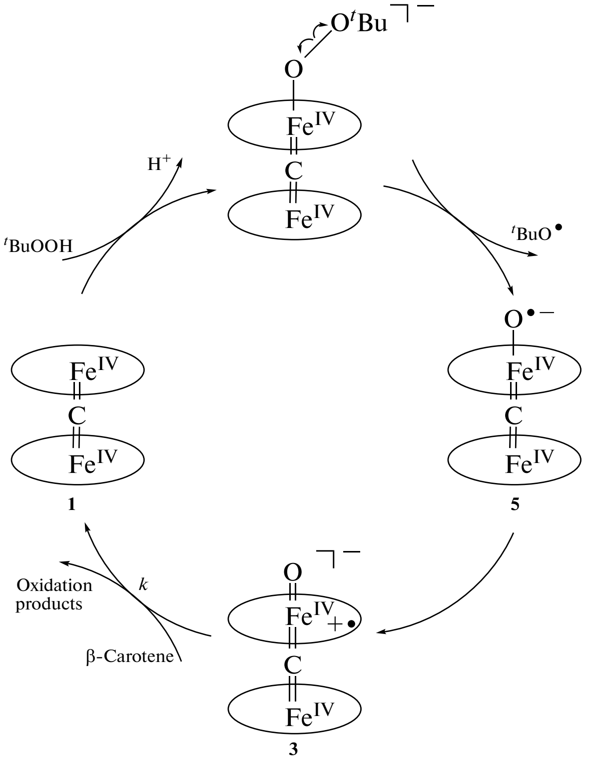


Fig. 2. IR spectra of (*a*) compound **3**, (*b*) **3**–β-carotene and (*c*) compound **4**. The point marks vibrations of π radical cation form.

N-bases in the coordination sphere of the iron complex studies on the rate of formation and the form of the active species in the oxidative destruction of β-carotene, the reaction was studied with the participation of compound **4**, which is the oxidized form of the axial complex **2**.

The introduction of imidazole molecules into the coordination sphere of complex **1** leads to the formation of compound **2** (Fig. 4, line *1*) [31], which is analogous to axial μ-carbido diiron(IV) macrocyclic complexes studied earlier [28, 29]. The addition of ^{t}BuOOH ($C_{^t\mathrm{BuOOH}} = 8.6 \times 10^{-3}$ mol/L) to the solution of compound **2** in benzene leads to its oxidation (compound **4**) and is accompanied by changes in the EAS shown in Fig. 4 (lines *1* and *2*). However, the maximums of the spectral line *2*, which corresponds to the oxidized form **4** do not coincide with those of the π radical cation form **3** (Fig. 1, line *2*), and in the IR spectrum of the complex, the band corresponding to the vibration of the form oxidized at the macrocycle is absent (Fig. 2, *c*). Moreover, when detecting form **4** by spectral methods, the solution starts to drill, which points to the evolution of O_2. When adding β-carotene to the solution, it decolorizes for 80 s ($k \approx 25$ L^2 mol^{-2} s^{-1}). The kinetics of β-carotene decomposition in the presence of compound **4** was studied in the range of measurable rates at a lower concentration of ^{t}BuOOH ($C_{^t\mathrm{BuOOH}} = 2.3 \times 10^{-3}$ mol/L). The linear dependence of apparent rate constants of the reaction of formal first order ($\log k_{\mathrm{app}}$) for **4**–β-carotene–benzene system (correlation equation $\log k_{\mathrm{app}} = 1.019 + 0.992 \log C_{\mathrm{Car}}$, $R^2 = 0.999$) has $\tan \alpha = 1$. The second-order rate constant k in the rate equation analogous to Eq. (1) with C_4 instead of C_3 is 10.3 L^2 mol^{-2} s^{-1}, which is three times higher than that of the reaction with compound **3**. β-Carotene added to the reaction mixture upon the reaction completion is also decolorized, similarly to the reaction with the participation of compound **3.** However, after several cycles, the rate of the process gradually decreases, which is evident from a decrease in the apparent constant k_{app} (Fig. 3b).



Scheme 1.

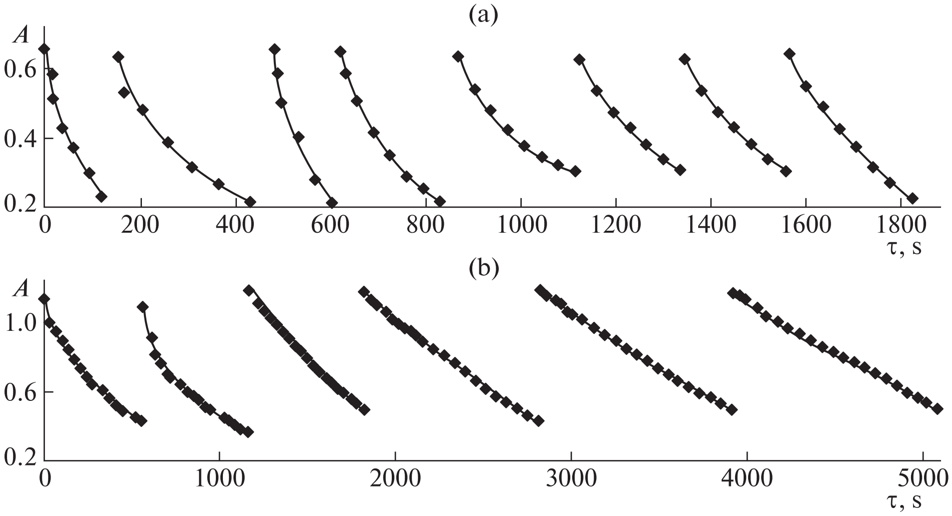


Fig. 3. Kinetic curves for the reaction of oxidative decomposition of β-carotene in the presence of (a) compound **3** and (b) compound **4** when the substrate is periodically added to the reaction mixture.

The role of N-bases coordinated by metal, which stabilize highly covalent forms of both monomeric and dimeric macrocyclic and nonheme iron complexes in increasing the reactivity and catalytic activity of these compounds in oxidation reactions is described well in the literature [23, 28, 31–36]. However, the reaction features and spectral data shown in Figs. 1 and 4 point to the participation of carotene in the oxidation of various active forms of complexes **1** and **2**. If in the case of compound **1**, form **3** stable in the solution and oxidized at a macrocyclic ligand (Fig. 2b) participates in the reaction, the position of bands in the EAS for compound **4** (414 and 609 nm) does not allow one to identify it as a singly oxidized π radical cation form. It is obvious that compound **4** is so active that it can oxidize ^{t}BuOOH to form O_2 analogously to oxidized forms of some monomeric and dimeric porphyrin complexes of iron(IV) [37, 38].

According to the references data, μ-carbido diiron(IV) complexes with tetraazaporphyrin, tetraphenylporphyrin, phthalocyanine, and tetra-(tert-butyl)phthalocyanine (homo- and heteroleptic) can be subjected to two one-electron oxidations electrochemically [7, 23, 33, 39]. The product of the first oxidation in all cases is a radical cation with a positive charge localized on one of the macrocyclic ligands, and the product of the second oxidation was not identified. Only in the case of $(FeTAP)_2C$ two processes with potentials in the positive range were assigned to consecutive oxidations of two macrocycles in the complex with the formation of π radical dication [7]. The other highly covalent species can be the oxo form of the Fe^{4+} complex with the localization of a positive charge on one of the macrocyclic ligands and a radical on the bridging carbon atom. The hypothetical geometric and electronic structure of such a species was calculated by the DFT method for $(FePc)_2C$ in [40], but there are no experimental data that support the proposed structure. When studying the oxidation reactions of monomeric iron complexes with corroles, corrolazines, and porphyrins and their catalytic roles in oxidation of various substrates, reaction schemes were proposed that involve the participation of oxo forms of iron(V) [41–45]. The method of laser photolysis was used to oxidize iron(IV) 5,10,15-tri(pentafluorophenyl)(chlorato)corrolate (O_2ClO)FePFPC in CH_3CN with the formation of short-lived reactive intermediate that was detected by spectrophotometry [46]. Based on its unique EAS, which differed from the spectrum of π radical cation, and the high reactivity, the authors denoted this species as an oxo complex of iron(V). The latter is isoelectronic to singly oxidized

Table 1. The products of β-carotene oxidation identified by the ESI–MS method after the reaction in the presence of compounds **3** and **4**

Compound	$[M^+]$
Ionone	174
8-Apo-β-carotenal	166
5,6-Epoxy-β-ionone	208
Dihydroactinidiolide*	180
10'-Apo-β-carotenal	208
β-Cyclocitral	377
β-Ionone	392
Criegee biradical	152
12'-Apo-β-carotenal biradical	192
7-Apo-β-carotenal biradical	184

* Present only after reaction with the participation of compound **4.**

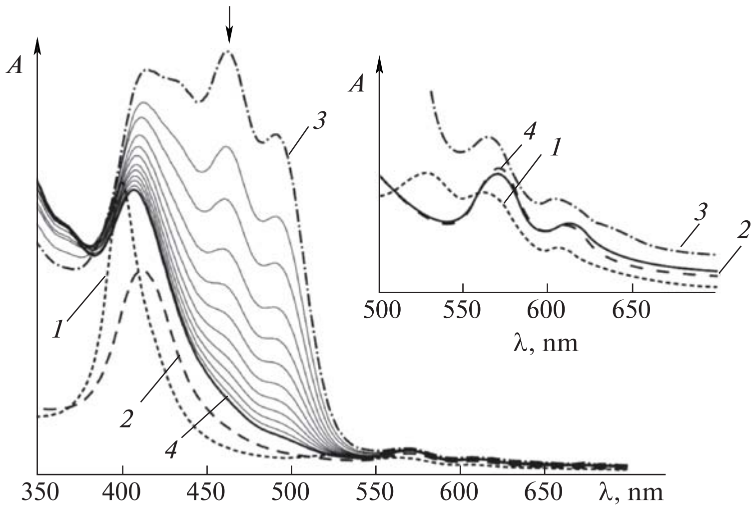


Fig. 4. Electron absorption spectra of compounds in benzene: (*1*) compound **2** and (*2*) compound **4** ($C_{{}^t\mathrm{BuOOH}} = 2.3 \times 10^{-3}$ mol/L); (*3*) compound **4** after adding β-carotene ($C_{\mathrm{Car}} = 4.3 \times 10^{-4}$ mol/L); (*4*) the same as *3* upon reaction completion.

isomer of complex $\mathrm{O{=}Fe^{IV}P^{+\bullet}}$, which is more reactive than $\mathrm{O{=}Fe^{IV}P^{+\bullet}}$.

The EAS of the active intermediate **4**, which we managed to detect, is similar to that of the compound studied in [46]. However, short lifetime prevents compound **4** from isolation and reliable identification by other physical methods.

When comparing the oxidative properties of oxo forms $(\mathrm{FePc})_2\mathrm{X}$ (X = O, N, C) the authors of [40] noted a much higher reactivity of nitrido-dimeric complexes based on the very high covalence of the axial Fe–N bond in a series of X-bridging structures and on the *trans*-effect of the N-bridge, which weakened the Fe–O bond and accelerated the formation of highly oxidized species. The axially bridged imidazole, being an electron-donor N-base, has an analogous effect in compound **2** when generating the reactive form **4** in reaction with ^{t}BuOOH by increasing the rate of its formation in the homolytic cleavage of the O–O bond [32, 34, 36]. The nature of compound **4** is a subject of further study. Obviously high reactivity of compounds **3** and **4**, which activate the process of oxidative destruction of β-carotene, makes it possible to consider them as promising catalysts of oxidation processes and models of natural peroxidases.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 15-03-04327-a). IR spectral studies were performed at the Shared Resource Center *Verkhnevolzhskii Regional Center for Physicochemical Studies*.

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Translated by A. Zeigarnik