Reaction of substituted iron phthalocyanines with dioxygen in acidic medium

1. Oxidation of iron 5,5′,5″,5‴-tetra(*tert*-butyl)-3,3′,3″,3‴-tetra(phenylthio)phthalocyanine

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The reaction of acidic form of the substituted iron phthalocyanine complex (3-PhS-5-Bu^t)$_4$pc′Fe (pc″Fe) with dioxygen in *o*-dichlorobenzene in the presence of dichloroacetic acid (HX) was investigated. The oxidation of Hpc″FeX gives the corresponding radical cation, which was confirmed by the stoichiometry of reduction of the product formed in this reaction with a two-electron reducing agent. The kinetic equation obtained on the basis of dependences of the oxidation rate on the Hpc″FeX, HX, and O_2 concentrations are consistent with the reaction mechanism that implies the formation of a Hpc″FeX complex with O_2 and its transformation to give a radical cation under the action of HX.

Key words: iron phthalocyanine, oxidation, dioxygen, catalysis.

The problem of creation of oxidative systems simulating the functions of heme oxidases, in particular, oxygenases, is fairly topical for the development of effective environmentally safe oxidation processes. The known chemical models of cytochrome P-450, for example, TpivPPFeBr—Zn(Hg)—MV^{2+}—Ac_2O—O_2 (TpivPP is α,α,α,α-*meso*-tetrakis(*ortho*-pivaloylphenyl)porphyrin, MV is methylviologen)[1] contain iron porphyrin (P) derivatives as catalysts, which form ferryl type active species, $P^{\bullet+}Fe^{IV}{=}O$ or $PFe^{IV}{=}O$, during oxidation. These species react subsequently with the substrates. The proportion of the products formed by a radical mechanism does not exceed 20%.[2,3] However, due to complexity of the synthesis, these models have no prospects in the development of practically valuable catalyst systems. This accounts for the interest in the study of iron phthalocyanine (pcFe), the aza analog of porphyrins, and catalytic oxidation of organic substrates using phthalocyanine catalysts.[4—7] This interest is due, on the one hand, to high catalytic activity of pcFe in oxidation and, on the other hand, to the ready availability and relatively high stability of phthalocyanines and their substituted derivatives.[8] Previously, attempts to use azaporphins for modeling of the active sites of heme oxidases have been made only occasionally. This is also true for modeling of the total enzyme system of monooxygenases, in which dioxygen itself acts as the oxidant, rather than the shunted one, which makes use of reduced forms of oxygen. It is quite obvious that the problem of the nature and the efficiency of the interaction of azaporphin, for example, pcFe, with oxygen is the central point.

Unlike iron porphyrins, which react with oxygen with oxidation of the Fe atom and, if no special substituents are introduced, to give Fe^{III} μ-oxo dimers,[9] iron phthalocyanines form, in neutral organic media, rather stable μ-oxo dimers that are believed to be Fe^{II} derivatives of the type HpcFe—O—FepcH.[10] It has been also suggested[11] that these products are Fe^{III} derivatives, structural analogs of the corresponding porphyrins. No definite data on the reactions of substituted pcFe with oxygen in neutral aqueous media have been obtained so far.[12]

In acid media, iron(II) porphyrin complexes are oxidized with dioxygen to PFeX (X = Cl).[9] The reaction of pcFe with oxygen in the presence of acids has scarcely been studied, although substituted pcFe are effective catalysts for oxidation of, for example, aromatic amines, with oxygen or hydrogen peroxide exactly in acid media.[8,13]

Previously, we found[14] that substituted pcFe containing electron-releasing or weak electron-withdrawing substituents (Bu^t, PhO, PhS) efficiently react with oxygen in acidic solutions in which they exist in so-called acidic forms.[15,16] This is indicated by a decrease in the solution absorbance at the wavelength of the phthalocyanine Q-band. The introduction of strong electron-withdrawing groups ($PhSO_2$, Bu_2NSO_2) into the pcFe molecule makes the complex inert toward oxygen; in any case, this

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interaction cannot be detected by spectroscopy. The effect of the nature of substituents in the $HR_4pc'FeX$ complexes on the rate of oxidation with oxygen (W_0/mol L^{-1} s^{-1}) is shown below ($[HR_4pc'FeX]_0$ = $1.4 \cdot 10^{-5}$ mol L^{-1}, $[HX]_0$ = $5 \cdot 10^{-3}$ mol L^{-1}, 25 °C, *o*-dichlorobenzene (DCB), air).

R	3-PhS-5-Bu^t	4-PhO	4-Bu^t	4-PhS	3-*o*-ClC$_6$H$_4$
$W_0 \cdot 10^9$	5.0	1.43	0.9	0.7	0.1

This study deals with the stoichiometry, kinetics, and mechanism of the interaction of pcFe derivatives with dioxygen using the most active of the considered complexes, (3-PhS-5-Bu^t)$_4$pc′Fe (pc″Fe), in a DCB—dichloroacetic acid (HX) solution, as an example. The choice of the complex containing simultaneously both the Bu^t group and a bulky substituent in position 3 of the benzene ring attached to the macrocycle allows one to avoid complications related to the aggregation of phthalocyanines and the possible presence of positional isomers, which could be formed during the synthesis of phthalocyanines from 4-substituted phthalogens.

It was found that pc″Fe existing as the acidic complex (Hpc″FeX) reacts rather actively with dioxygen to give the oxidized form. This reaction was monitored by spectroscopy based on a decrease in the absorbance of the solution at the absorption maximum of Hpc″FeX (706 nm) and an increase in the absorbance at 810 nm, the isosbestic points at 431, 741, 889, and 941 nm remaining intact, which indicates the absence of side processes (Fig. 1).

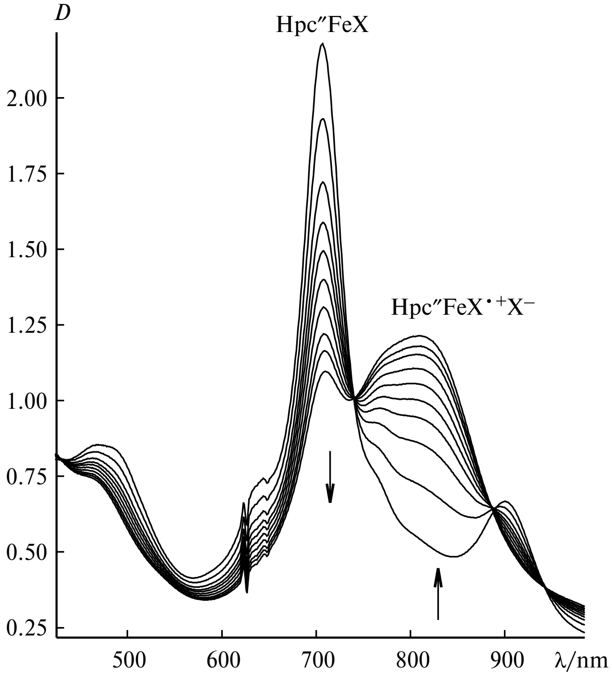

Fig. 1. Time variation of the absorption spectra of a solution of H(3-PhS-5-Bu^t)$_4$pc′FeX (Hpc″FeX) ($[Hpc''FeX]_0$ = $3 \cdot 10^{-5}$ mol L^{-1}, $[HX]_0$ = $5 \cdot 10^{-3}$ mol L^{-1}, $[O_2]_0$ = 100% (v/v), DCB).

Experimental

The complex (3-PhS-5-Bu^t)$_4$pc′Fe was synthesized as the μ-oxo dimer by a previously described procedure.[17] *o*-Dichlorobenzene was purified on a column with Al_2O_3 (Brockmann neutral) followed by distillation *in vacuo* in a flow of argon. Dichloroacetic acid was distilled *in vacuo*. Commercial $PhI(OAc)_2$ was used (Aldrich).

Procedure for kinetic measurements. The kinetic studies were carried out on an HP-845x UV-Vis spectrophotometer at 25 °C in a quartz cell with a layer thickness of 1 or 0.5 cm. The oxygen content in nitrogen—oxygen gas mixtures was determined on a Tsvet chromatograph (5 Å molecular sieves; helium as the carrier gas; temperature of the column thermostat, 60 °C; temperature of the chamber and detector, 70 °C). Prior to mixing, solutions of the pc″Fe μ-oxo dimer and HX in DCB were purged with a gas mixture dried by passing through calcined molecular sieves. The initial oxidation rate was determined by differentiating the curves for time variation of the concentration of Hpc″FeX for $\tau = 0$.

Procedure for determining the process stoichiometry. A mixture of solutions of the pc″Fe μ-oxo dimer ($1.4 \cdot 10^{-5}$ mol L^{-1}) and HX ($5 \cdot 10^{-3}$ mol L^{-1}) in DCB was kept in the dark at ~20 °C for 2, 3, and 15 h. After a specified time period, the absorption spectrum of the solution was recorded and the concentrations of the starting (Hpc″FeX (**A**)) and final (Hpc″FeX$^{\cdot+}$X$^-$ (**B**)) forms were determined from the relations

$$C_{\mathbf{A}} = (D^a - D^b\varepsilon_{\mathbf{B}}{}^a/\varepsilon_{\mathbf{B}}{}^b)/(\varepsilon_{\mathbf{A}}{}^a - \varepsilon_{\mathbf{B}}{}^a\varepsilon_{\mathbf{A}}{}^b/\varepsilon_{\mathbf{B}}{}^b),$$

$$C_{\mathbf{B}} = (D^b - D^a\varepsilon_{\mathbf{A}}{}^b/\varepsilon_{\mathbf{A}}{}^a)/(\varepsilon_{\mathbf{B}}{}^b - \varepsilon_{\mathbf{A}}{}^b\varepsilon_{\mathbf{B}}{}^a/\varepsilon_{\mathbf{A}}{}^a),$$

where D^a and D^b are the absorbancies of the solution at 706 and 810 nm, respectively; $\varepsilon_{\mathbf{A}}$ and $\varepsilon_{\mathbf{B}}$ are the molar extinction coefficients of the starting and final forms of the phthalocyanine complexes: $\varepsilon_{\mathbf{A}}{}^a = 0.788 \cdot 10^5$, $\varepsilon_{\mathbf{A}}{}^b = 0.113 \cdot 10^5$, $\varepsilon_{\mathbf{B}}{}^a = 0.196 \cdot 10^5$, $\varepsilon_{\mathbf{B}}{}^b = 0.407 \cdot 10^5$ L mol^{-1} cm^{-1} (the $\varepsilon_{\mathbf{B}}{}^a$ and $\varepsilon_{\mathbf{B}}{}^b$ values were determined using $PhI(OAc)_2$ as the oxidant to attain complete conversion of Hpc″FeX into the oxidized form). Dioxygen was removed from the solution by bubbling argon for 1 h. A solution of the reducing agent (leuco base of crystal violet, DH) freed from O_2 was added to an O_2-free mixture of Hpc″FeX and the reaction product, the cell was sealed, and the absorbancies of the solution at 706 (Hpc″FeX), 810 (Hpc″FeX$^{\cdot+}$X$^-$), and 595 nm (oxidized form of the reducing agent, the D$^+$X$^-$ dye) were monitored (Fig. 2).

The concentrations of D$^+$X$^-$ were calculated from the equation

$$C_{D^+X^-} = (D^c - D^a\varepsilon_{\mathbf{A}}{}^c/\varepsilon_{\mathbf{A}}{}^a)/(\varepsilon^c_{D^+X^-} \cdot l),$$

where D^c is the absorbance of the solution at 595 nm; $\varepsilon_{\mathbf{A}}{}^c$ is the molar extinction coefficient of the complex Hpc″FeX at 595 nm, equal to $0.0875 \cdot 10^5$ L mol^{-1} cm^{-1}; $\varepsilon^c_{D^+X^-} = 1.0 \cdot 10^5$ L mol^{-1} cm^{-1}; and *l* is the layer thickness (1 cm). The results are presented in Table 1.

Table 1. Stoichiometric parameters of the reduction of the (3-PhS-5-Bu^t)$_4$pc´Fe radical cation[a]

Time[b] /h	Before the reduction			After the reduction			$C_{\text{Hpc''FeX}^{\bullet+}\text{X}^-}$/ /$C_{\text{D}^+\text{X}^-}$
	$C_{\text{Hpc''FeX}^{\bullet+}\text{X}^-}$	$C_{\text{Hpc''FeX}}$	$\Sigma C_{\text{pc''Fe}}$[c]	$C_{\text{Hpc''FeX}}\cdot 10^5$ /mol L^{-1}	Irreversible destruction (%)	$C_{\text{D}^+\text{X}^-}\cdot 10^5$ /mol L^{-1}	
	$\cdot 10^5$/mol L^{-1}						
2	0.73	0.40	1.13	1.09	22	0.42	1.7
3	0.81	0.30	1.11	1.10	21	0.39	2.1
15	0.96	0.16	1.12	1.07	24	0.51	1.9

[a] $[\text{Hpc''FeX}]_0 = 1.4\cdot 10^{-5}$ mol L^{-1}, $[\text{HX}]_0 = 5\cdot 10^{-3}$ mol L^{-1}, and $[\text{DH}]_0 = 2\cdot 10^{-5}$ mol L^{-1}.

[b] Duration of keeping the solution of Hpc″FeX in air.

[c] $\Sigma C_{\text{pc''Fe}} = C_{\text{Hpc''FeX}^{\bullet+}\text{X}^-} + C_{\text{Hpc''FeX}}$.

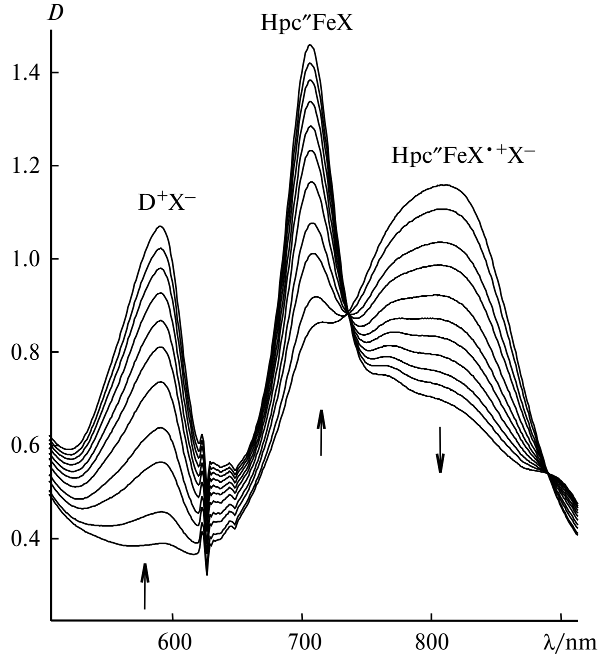

Fig. 2. Reduction of Hpc″FeX$^{\bullet+}$X$^-$ in the presence of DH with time at $[\text{HpcFeX}^{+\bullet}\text{X}^-]_0 = 3\cdot 10^{-5}$ mol L^{-1}, $[\text{DH}]_0 = 2\cdot 10^{-5}$ mol L^{-1}, $[\text{HX}]_0 = 5\cdot 10^{-3}$ mol L^{-1}.

Results and Discussion

We will start with the discussion of the possible nature of the products formed in the reaction between the acidic complex Hpc″FeX and oxygen and the reaction stoichiometry. The only reaction product exhibits a characteristic electronic absorption spectrum with the major absorption band at 810 nm (see Fig. 1). Comparison of this spectrum with the reported spectra of the radical cations derived from metal phthalocyanines[18,19] provides data for assuming that the oxidation of Hpc″FeX with dioxygen affords a radical cation with a hole located on the phthalocyanine macro ring. The oxidation of the central atom would have resulted in only a slight shift of the long-wavelength absorption band with almost no change in the spectral structure or band shape.[19—21] The fact that the action of reducing agents (hydroquinone, DH) on the reaction product under argon results in almost complete recovery of Hpc″FeX is in line with this hypothesis. When DH is used as the reducing agent, a well-known dye whose concentration in this system can be easily determined by spectroscopy is formed upon its oxidation. This was used to determine the reduction stoichiometry and, as a consequence, the stoichiometry of the oxidation of the starting complex with dioxygen. It was found that regeneration of 1 mole of Hpc″FeX requires ~0.5 mole of a two-electron reducing agent, in this particular case, DH. This fact, together with spectral data implies that oxidation occurs as a one-electron process and that the macroligand rather than the central metal atom functions as the reaction center. Note that within the framework of the views on the iron(II) oxidation state in acidic complexes,[22,10] the oxidation of the macro ring with dioxygen indicates specific properties of the phthalocyanine complexes compared to porphyrin analogs.

$$\text{Hpc''FeX} + \text{O}_2 + \text{HX} \longrightarrow \text{Hpc''FeX}^{\bullet+}\text{X}^- + \text{HO}_2^{\bullet}$$

For discussing the possible intermediacy of the radical cation formed in the catalytic processes involving pcFe derivatives, not only the reduction stoichiometry but also its kinetics is a relevant aspect. The study of the kinetic features of the reduction of Hpc″FeX$^{\bullet+}$X$^-$ with DH under argon demonstrated that the reduction rate obeys first-order kinetics with respect to concentrations of both reactants (Figs 3, 4)

$$W_{\text{D}^+\text{X}^-} = k_1\cdot[\text{Hpc''FeX}^{\bullet+}\text{X}^-]\cdot[\text{DH}],$$

where $k_1 = 2.3$ L mol^{-1} s^{-1}. This suggests the following reaction route:

$$\text{Hpc''FeX}^{\bullet+}\text{X}^- + \text{DH} \longrightarrow \text{Hpc''FeX} + \text{D}^{\bullet} + \text{HX}, \qquad (1)$$

$$\text{Hpc''FeX}^{\bullet+}\text{X}^- + \text{D}^{\bullet} \longrightarrow \text{Hpc''FeX} + \text{D}^+\text{X}^-. \qquad (2)$$

Now we turn back to the main process, namely, the oxidation of the acidic form of pc″Fe with dioxygen. The

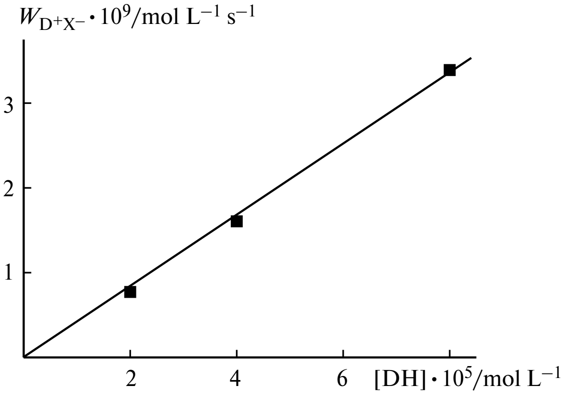

Fig. 3. Rate of oxidation of DH ($W_{D^+X^-}$) with the Hpc″FeX$^{\bullet+}$X$^-$ radical cation *vs.* DH concentration ([Hpc″FeX$^{\bullet+}$X$^-$]$_0$ = 1.8$\cdot$10^{-5} mol L^{-1}, [HX]$_0$ = 5$\cdot$10^{-3} mol L^{-1}).

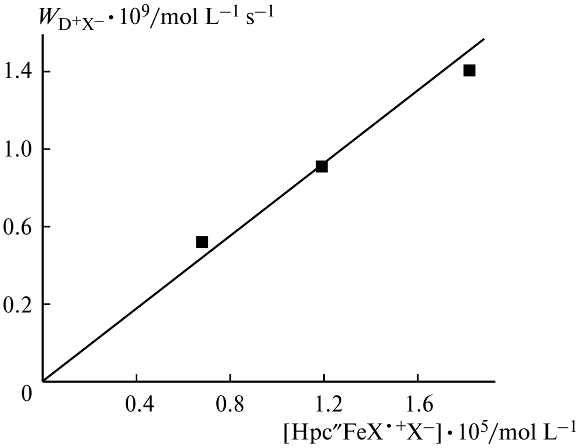

Fig. 4. Rate of oxidation of DH ($W_{D^+X^-}$) with the Hpc″FeX$^{\bullet+}$X$^-$ radical cation *vs.* Hpc″FeX$^{\bullet+}$X$^-$ concentration ([DH]$_0$ = 4$\cdot$10^{-5} mol L^{-1}, [HX]$_0$ = 5$\cdot$10^{-3} mol L^{-1}).

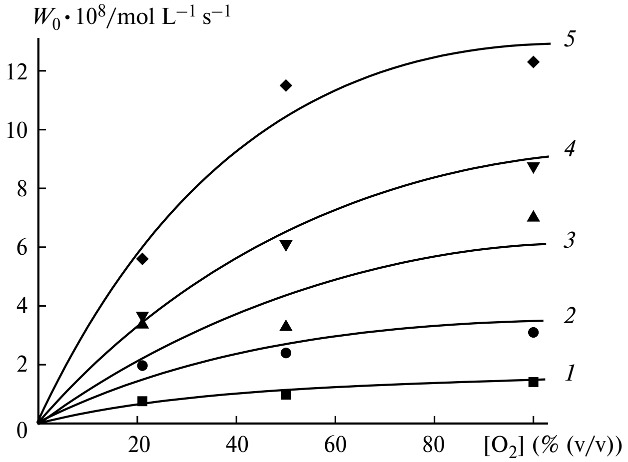

Fig. 5. Rate of oxidation of Hpc″FeX (W_0) *vs.* partial pressure of oxygen at different concentrations of the complex: [Hpc″FeX]$_0\cdot$10^5 = 1.4 (*1*), 3.0 (*2*), 6.0 (*3*), 8.0 (*4*), and 12.0 mol L^{-1} (*5*) ([HX]$_0$ = 5$\cdot$10^{-3} mol L^{-1}).

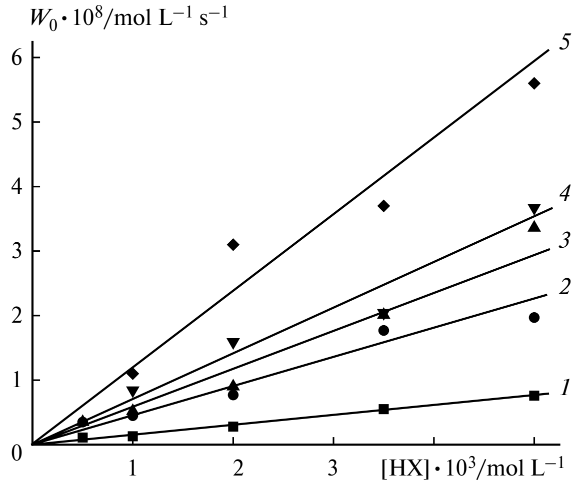

Fig. 6. Rate of oxidation of Hpc″FeX (W_0) *vs.* [HX] at different concentrations of the complex: [Hpc″FeX]$_0\cdot$10^5 = 1.4 (*1*), 3.0 (*2*), 6.0 (*3*), 8.0 (*4*), and 12.0 mol L^{-1} (*5*) ([O$_2$]$_0$ = 21% (v/v)).

kinetic measurements were carried out over a broad range of concentrations of the starting complex ((1.4—12.0)$\cdot$10^{-5} mol L^{-1}), dichloroacetic acid ((0.5—5.0)$\cdot$10^{-3} mol L^{-1}), and oxygen (O$_2$ content in the gas used to saturate the solution prior to the experiment was 10—100% (v/v)). The partial dependences of the reaction rate measured from the consumption of Hpc″FeX on the reactant concentrations are shown in Figs 5—7, and the graphical processing of the whole set of kinetic data is presented in Fig. 8. It can be seen that the experimental plots are described satisfactorily by the equation

$$W_{\mathrm{exp}} = (A[\mathrm{Hpc''FeX}][\mathrm{O_2}][\mathrm{HX}])/(1 + B[\mathrm{O_2}]), \qquad (3)$$

where A and B are constants.

This is not at variance with the stepwise oxidation scheme, according to which the Hpc″FeX complex with O$_2$ formed in the first step reacts with HX to give the corresponding radical cation.

$$\mathrm{Hpc''FeX} + \mathrm{O_2} \underset{}{\overset{K}{\rightleftarrows}} \mathrm{Hpc''FeX...O_2} \qquad (4)$$

$$\mathrm{Hpc''FeX...O_2} + \mathrm{HX} \xrightarrow{k_2} \mathrm{Hpc''FeX^{\bullet +}X^-} + \mathrm{HO_2}^{\bullet} \qquad (5)$$

Expression (6) derived from Eqs (4) and (5) for [O$_2$] >> [Hpc″FeX] (solubility of oxygen in DCB is 1.3$\cdot$10^{-3} mol L^{-1})

$$W = (k_2K[\mathrm{Hpc''FeX}][\mathrm{O_2}][\mathrm{HX}])/(1 + K[\mathrm{O_2}]), \qquad (6)$$

where K is the equilibrium constant, agrees with the experimental equation (3) when $A = k_2K$, $B = K$,

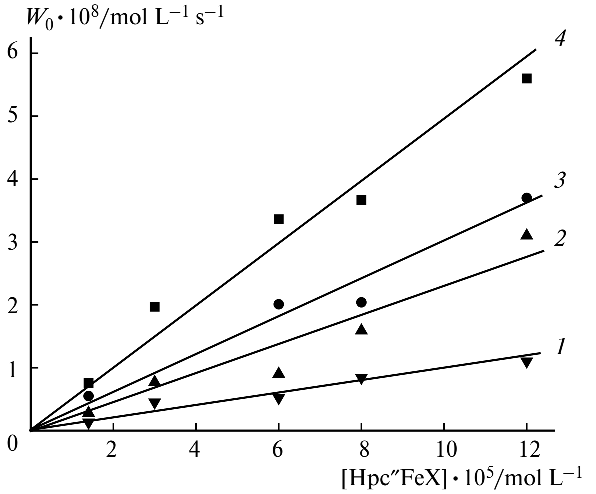

Fig. 7. Rate of oxidation of Hpc″FeX (W_0) *vs.* its concentration at different [HX]: $[HX]_0 \cdot 10^5$ = 1.0 (*1*), 2.0 (*2*), 3.5 (*3*), and 5.0 mol L^{-1} (*4*) ($[O_2]_0$ = 21% (v/v)).

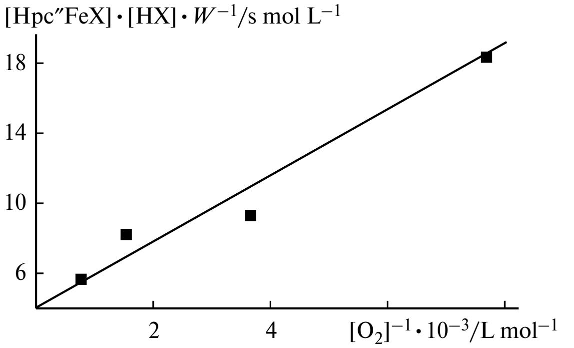

Fig. 8. Dependence of the [Hpc″FeX] · [HX] · W^{-1} value (W is the arithmetic mean of at least five experimental W_0 values) on $[O_2]^{-1}$.

k_2 = 0.25 L mol^{-1} s^{-1}, $K = 0.21 \cdot 10^4$ L mol^{-1} (for comparison, for $(F_8TPP)Fe^{II}$, $K = (3\pm2) \cdot 10$ L mol^{-1} (EtCN),[23] for methmyoglobin, $K = 8.1 \cdot 10^5$ L mol^{-1} [24]).

According to Eq. (5), the oxidation of Hpc″FeX with oxygen affords the $HO_2^{\bullet}$ radical. Previously, the $O_2^{\bullet-}$ radical anions have been found to arise[25] in the self-oxidation of a number of cytochromes. To estimate the degree of participation of the $HO_2^{\bullet}$ radical in the oxidation of the Hpc″FeX complex, radical inhibitors were used, namely, 2,2,6,6-tetramethyl-4-benzoyloxypiperidin-*N*-oxyl (AmO$^{\bullet}$) ($1 \cdot 10^{-5}$—$5 \cdot 10^{-3}$ mol L^{-1}) and *p*-nitrosodimethylaniline (NDA) ($5 \cdot 10^{-5}$—$5 \cdot 10^{-3}$ mol L^{-1}). The effect of AmO$^{\bullet}$ is based on its ability to accomplish repeated chain termination through a cyclic mechanism.[26]

$$\mathrm{AmO}^{\bullet} + \mathrm{HO_2}^{\bullet} \longrightarrow \mathrm{AmOH} + \mathrm{O_2} \qquad (7)$$

$$\mathrm{AmOH} + \mathrm{HO_2}^{\bullet} \longrightarrow \mathrm{AmO}^{\bullet} + \mathrm{H_2O_2} \qquad (8)$$

The introduction of AmO$^{\bullet}$ and NDA in concentrations [AmO$^{\bullet}$] < $1 \cdot 10^{-4}$ mol L^{-1} and [NDA] < $5 \cdot 10^{-4}$ mol L^{-1} into a solution of Hpc″FeX ($3 \cdot 10^{-5}$ mol L^{-1}) and HX ($5 \cdot 10^{-3}$ mol L^{-1}) has virtually no influence on the oxidation rate of Hpc″FeX with dioxygen in DCB, which implies an insignificant participation of free radicals in the process. This fact is due to the consumption of the $HO_2^{\bullet}$ radicals in side reactions, similarly to that observed in the Fenton system according to the modern views.[27]

An increase in the inhibitor concentrations above the above-indicated values induces effects acting in the opposite directions, which are of interest as regards the functioning of phthalocyanines as oxidation catalysts. At higher concentrations of AmO$^{\bullet}$, the consumption of Hpc″FeX is sharply accelerated, which is probably due to the formation of H_2O_2 according to reaction (8). The catalytic decomposition of this compound gives rise to the OH$^{\bullet}$ radicals and, hence, it is accompanied by the destruction of the phthalocyanine complex. An increase in the [NDA] to $5 \cdot 10^{-3}$ mol L^{-1} results, conversely, in complete retardation of the reaction. One reason is the nonproductive complexation of Hpc″FeX with NDA, similar to that taking place in the presence of, for example, pyridine,[21] as indicated by the red shift of the absorption maximum of the solution (706 nm → 722 nm). In addition, the reduction of the radical cation with the inhibitor found in an independent experiment also makes a contribution.

Thus, we found that the coordination of the acidic complex formed by substituted iron phthalocyanine to dioxygen results in a substantial activation of the latter and enable complete electron transfer from the macro ring to oxygen to give the corresponding radical cation. This bears an analogy with the combustion of crystalline iron phthalocyanine in air at elevated temperatures.[28]

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