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Reaction of Iron Phthalocyanine with Oxygen: Critical Survey and New Data on the Structure of the Forming PcFe(II) μ-Oxo Dimer

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Abstract—Reaction of iron tetra-4-tert-butylphthalocyanine (Pc^tFe) with oxygen in noncoordinating solvents at Pc^tFe concentrations within $(0.63–10.71) \times 10^{-2}$ M was studied. The uptake of oxygen (moles per mole of iron phthalocyanine taken into reaction) depends on the concentration of the complex, varying in the examined concentration range from 1/5 to 1/2.7, and thus can significantly differ from the value implied by the stoichiometry of the Pc^tFe μ-oxo dimer. This fact is due to consumption of the reactants in side processes, including oxidative degradation of the macroring. Indeed, the μ-oxo dimer is the major but not the only product of reaction of Pc^tFe with oxygen: Up to 20% of the initial complex undergoes oxidative degradation. These data, in combination with the spectral and chemical properties of the Pc^tFe μ-oxo dimer, suggest that this compound is an Fe(2+) derivative.

During the past 15–20 years, in papers concerning catalytic properties of metal azaporphine complexes a particular attention was given to iron phthalocyanine (PcFe) and its substituted derivatives (R_nPcFe). This is due not only to the high catalytic activity of these compounds, mainly in oxidation processes [1–8] (this property has been known for a long time), but also to realization of unique possibilities furnished by the structure of PcFe and making it promising as a model of active centers of heme-containing proteins. Today, thanks to advances in synthetic chemistry of phthalocyanines, many substituted derivatives of PcFe became accessible by preparative synthesis, which provides an opportunity for mild modification of the molecule by introducing substituents with widely varied steric and electronic characteristics in the periphery of the macroring [9–12]. In this connection, study of the coordination chemistry of iron phthalocyanine, in particular, of products of its reaction with molecular oxygen, can become an important step in modeling the functions of natural hemoproteins.

At the same time, in the literature concerning PcFe applied papers apparently prevail over works directly aimed at studying the reactions of R_nPcFe or PcFe with O_2 and their products. In available publications, experiments have been performed either with unsubstituted PcFe or with its sulfo derivatives. Such a choice of the investigation objects, as will be shown below, leads to significant problems with data interpretation.

In 1965, Fallab *et al.* [13] reported the reversible binding of oxygen with tetrasulfonated iron phthalocyanine (TSPcFe) in a neutral aqueous solution with formation of a μ-peroxo dimer [13]. The reversibility of the reaction of TsPcFe with O_2 was questioned in [14] where it was stated, in accord with [15], that under the action of oxygen TSPcFe(2+) (λ_{max} 670 nm) is irreversibly oxidized to TSPcFe(3+) (λ_{max} 630 nm). However, Sigel *et al.* [16] found that interconversion of species responsible for the absorption maxima at 630 and 670 nm occurs in the absence of oxygen also, at varying temperature or concentration. Such a behavior suggests aggregation of TSPcFe—a process typical of Pc sulfo derivatives in aqueous solutions. These results cast doubt on the conclusion that TSPcFe(2+) is oxidized to TSPcFe(3+). The products of reaction of sulfonated PcFe with oxygen in the cited works were not isolated and characterized. Interaction of TSPcFe and PcFe with O_2 was also studied in acid solutions [17, 18]. However, azaporphines, and in particular PcFe, can interact with acids to give complexes of the type PcFe·HX and four species protonated at meso nitrogen atoms [19–21], so that actually different compounds were dealt with. In combination with possible aggregation, this fact severely complicates interpretation of the results.

Reaction of unsubstituted PcFe with O_2 was further studied in [22–27]. In 1979, Collamati reported the preparation of a stable oxygen-containing dimeric product by reaction of a suspension of PcFe in DMF with O_2. This product was identified as the μ-peroxo dimer PcFe–O–O–FePc [22]. However, soon after that this structure was rejected by Ercolani *et al*. [23] who proved that the bridge between the two iron atoms is the oxo rather than peroxo group. This conclusion was based on the IR spectrum of the ^{18}O-labeled analog and on the results of volumetric studies which showed that unsubstituted PcFe suspended in DMF takes up O_2 in the molar ratio $PcFe : O_2 = 4$. This fact was considered as a strong evidence of the formation of the μ-oxo dimer by reaction (1):

$$4PcFe(2+) + O_2 \longrightarrow 2PcFe(3+){-}O{-}Fe(3+)Pc. \quad (1)$$

By analogy with μ-oxo dimers of iron porphyrins, Ercolani *et al*. suggested for the reaction product the structure $[PcFe(3+)]_2O$ (hereinafter, structure **A**) with the iron oxidation state 3+. In the subsequent paper [26], Collamati agreed with this structure. It was also supported by Lever *et al*. [28] who prepared the tetra-(*N*-alkylsulfamide) analog of the PcFe μ-oxo dimer by chromatography of the corresponding substituted PcFe in air.

Study of the reaction of PcFe with oxygen is complicated by extremely low solubility of unsubstituted metal phthalocyanines in common solvents. It is not occasional that in [22–27] reactions of PcFe with oxygen to prepare the μ-oxo dimer were performed with suspensions of PcFe in coordinating solvents (dimethylacetamide, dimethylformamide, dimethyl sulfoxide, etc.). At the same time, the use of solvents fully inert toward PcFe is one of the necessary conditions for obtaining adequate data on reaction of iron phthalocyanine with oxygen. It should be noted that such a possibility did exist by the time when studies [22–27] were performed.

Taking into account the fact that introduction of *tert*-butyl groups into the periphery of phthalocyanine imparts to its metal complexes appreciable solubility in inert organic solvents, with the electronic properties of the system remaining virtually unchanged [29], we as early as 1975 [30] attempted to prepare iron tetra-4-*tert*-butylphthalocyanine (Pc^tFe) from the corresponding phthalonitrile and iron pentacarbonyl by the procedure [31] used for preparing unsubstituted PcFe. However, instead of Pc^tFe we obtained its stable oxygen-containing derivative which was readily (> 0.1 M) soluble in benzene and gave a characteristic visible absorption spectrum differing from the spectra of all the known coordination forms of iron phthalocyanine (λ_{max} 690 nm, ε 1.16×10^5 l mol^{-1} cm^{-1}, $\Delta\nu_{1/2}$ 1730 cm^{-1}). The compounds with the identical electronic spectrum was also prepared from unsubstituted PcFe (hereinafter this compound and its substituted analogs will be termed form 690) by heating in HCl-free *o*-dichlorobenzene at 60 – 65°C followed by precipitation of the arising form 690 from the filtrate with heptane. It should be emphasized that the necessary condition for preparing form 690 is a high (>10^{-3} M) concentration of PcFe in the suspension, since at lower (10^{-4}–10^{-5} M) concentrations of PcFe, under the same conditions, another species is formed, HPcFeCl [30].

The IR spectrum of isolated form 690 prepared from unsubstituted PcFe has characteristic bands at 820 and 856 cm^{-1}, which are reliably assigned [32] in iron porphyrin chemistry to antisymmetric vibrations of the Fe–O–Fe fragment. These results, in combination with analytical data, molecular weight measurements, and X-ray photoelectron spectra, allowed sufficiently reliable identification [30] of the oxygen-containing coordination forms of Pc^tFe and its unsubstituted analog as μ-oxo dimers, which by that time were unknown in the chemistry of iron phthalocyanine. The synthesis of Pc^tFe by the later developed [33] more convenient and efficient procedure involving reaction of 4-*tert*-butylphthalic anhydride with $FeBr_2$ and urea also yielded the μ-oxo dimer of Pc^tFe.

It is now clear that the formation of the μ-oxo dimer in attempted synthesis of R_nPcFe is not a specific property of tetra-4-*tert*-butyl-substituted PcFe. Data in [10, 12] show that this feature is characteristic of all iron phthalocyanines with substituents that exhibit moderate electronic effect and do not hinder sterically formation of the μ-oxo dimers. The difference between PcFe and its substituted analogs is that the former, owing to low solubility, precipitates from the reaction mixture under conditions of synthesis, whereas the substituted analogs in the course of synthesis and isolation, being in the dissolved state, react with ambient oxygen and moisture to give the corresponding μ-oxo dimers.

It should be noted that the presence of the fragment Fe–O–Fe in the oxygen-containing product of reaction of PcFe with O_2, reliably proved in [23], and the similarity of the electronic absorption spectra stimulated us to draw an analogy between this complex and the μ-oxo dimer of Pc^tFe, prepared, isolated, and characterized by us previously [30]. Unfortunately, this analogy was not given attention in such significant papers on reaction of PcFe with O_2 as [23, 26, 28].

The conclusion made in [23, 30] that form 690 is the μ-oxo dimer of PcFe or R_nPcFe was confirmed also in [10, 28, 34] and is beyond doubt. The problem of elucidating the iron oxidation state in this compound and correspondingly its detailed structure is more complicated. Even in our first study [30] concerning μ-oxo dimers of PcFe and Pc^{t}Fe, we considered alternative structures differing in the oxidation state of Fe: PcFe(3+)–O–Fe(3+)Pc (**A**) and HPcFe(2+)–O–Fe(2+)PcH (**B**), assuming and subsequently [21, 35, 36] substantiating that in the latter structure the hydrogen atoms are localized on the pyrrolenine nitrogen atoms of the phthalocyanine macrorings. We believed structure **B** to be more probable for these μ-oxo dimers, based on magnetic susceptibility data and ^{1}H NMR, Mössbauer, and X-ray photoelectron spectra of Pc^{t}Fe [35], suggesting the Fe oxidation state 2+ rather than 3+. This structure is also consistent with the chemical behavior of this dimer in reactions with acids and organic bases [21, 35, 36]. We isolated and characterized the final and intermediate products of these reactions, e.g., HPc^{t}FeCl, Py$_2$Pc^{t}Fe, ImH$^+$ · (Pc^{t}FeCl)$^-$ (Im is imidazole), and (ImH)$_2^+$[(Pc^{t}Fe)$_2$O]$^{2-}$. Structure **B** is also confirmed by the fact [36] that quantitative transformation of the μ-oxo dimer of Pc^{t}Fe into the bis-adduct with quinoline is accompanied by release of 1 mol of water per mole of the reacted dimer, and the amount of the released water does not decrease on addition to the reaction solution of triphenylphosphine as potential oxygen acceptor.

The dimer prepared by reaction of PcFe with O$_2$ and the other coordination derivatives of PcFe genealogically related to the μ-oxo dimer were actively studied by several research groups in different countries. Along with the above-cited papers, works [37–42] can be mentioned. Nevertheless, published structural data still do not allow unambiguous choice between structures **A** and **B**. This is largely due to the fact that, in contrast to the porphyrin analogs, numerous physicochemical studies of μ-oxo dimers of iron phthalocyanines (by UV-Vis absorption spectroscopy, magnetic susceptibility measurements, IR, X-ray photoelectron, ^{1}H and ^{13}C NMR, Mössbauer spectroscopy, etc.), summarized and correlated only recently [43], still leave room for doubts and ambiguous interpretations. In this connection, it seems urgent to study in detail the chemical properties of the μ-oxo dimers of PcFe and R$_n$PcFe, the more so as in many of the published papers this matter is not given due attention. It is possible that specifically analysis of the chemical properties, in combination with the results of physicochemical studies, will lead to progress in elucidating the structure of μ-oxo dimers of iron phthalocyanines. It should be emphasized that this problem is of practical significance for understanding and predicting the diversity of coordination species of R$_n$PcFe (and PcFe) in real solutions and on surfaces [9, 10, 35, 44], their reactivity, and the mechanism of the catalytic effect.

The characteristics and chemical properties given for form 690 suggest that in all the above-discussed papers, including our works, similar compounds were dealt with, irrespective of the preparation procedure, differing only in substituents in the macroring. Nevertheless, in the overwhelming majority of studies on the structure and properties of μ-oxo dimers of PcFe and its substituted derivatives the results are interpreted assuming structure **A**, whereas the alternative structure **B** is excluded from consideration without due substantiation. One of the probable reasons of rejecting structure **B** suggested by us is the lack of direct evidences of the presence of protons in the μ-oxo dimers. Up to now, these protons were not detected by any physicochemical methods, which is probably due to delocalization (more precisely, fast migration) of the proton over four internal nitrogen atoms of the macroring in each of the two phthalocyanine fragments [30, 35, 44]. Another cause of the continuing "coexistence" in the literature of the two structures of this compound, which is very important for the chemistry of iron phthalocyanine, is the published evidence of the strictly stoichiometric oxygen uptake [23] in formation of the μ-oxo dimer from PcFe and O$_2$ [reaction (1)] and of oxidative properties supposedly exhibited by the μ-oxo dimer [25].

The thorough experimental and theoretical analysis of these arguments is the major goal of this paper. First, let us consider in this context our new data on physicochemical properties of the μ-oxo dimer of Pc^{t}Fe.

In the ^{1}H NMR spectra of solutions of Pc^{t}Fe μ-oxo dimer, recorded at room temperature, the signals of the ring aromatic protons are observed in the range 9–10 ppm. With decreasing temperature to –60°C (solution in toluene), these signals shift downfield to 11–12 ppm. It is significant that similar changes in the ^{1}H NMR spectrum were observed in the course of reaction of the Pc^{t}Fe μ-oxo dimer with pyridine [reaction (2)] occurring, according to [24, 30, 35, 44, 45], via intermediate complex **D**, which is formed practically instantaneously (5–10 s) and then slowly transforms into bis-adduct **E**. Formation of the bis(pyridine) adduct is confirmed by the electronic absorption spectrum, elemental analysis of the solid sample isolated simply by solvent evaporation, and its Mössbauer spectrum (δ 0.518 mm s^{-1}, ΔE_Q 2.033 mm s^{-1} at 298 K) coinciding with that of the unsibstituted analog (Table 1).

Transformation (2) is manifested in the ^{1}H NMR

$$\underset{\substack{\mathbf{A}\\ 9\text{–}10\ \text{ppm}}}{(HPcFe)_2O} \xrightarrow{Py} \underset{\substack{\mathbf{D}\\ 11\text{–}12\ \text{ppm}}}{(PyH)_2^+[(PcFe)_2O]^{2-}} \xrightarrow{Py} \underset{\substack{\mathbf{E}\\ 8\text{–}9\ \text{ppm}}}{PcFe\cdot Py_2}. \qquad (2)$$

spectrum as fast shift of the signals of the macroring aromatic proton from 9–10 to 11–12 ppm followed by slow shift to 8–9 ppm. The latter range is typical of macroring protons in bis-adducts of type **E**; hence, these signals belong to the bis(pyridine) adduct as the final reaction product.

Taking into account also the sequence and time of changes observed in the ^1H NMR spectrum, we can confidently conclude that the signals in the range 11–12 ppm belong to the macroring protons in intermediate complex **D**. We believe that this complex is the ionized μ-oxo dimer of PcFe(2+). It should be reminded that the compound of type **D** detected in [30] and isolated and studied for the first time in [35], where it was prepared by reaction of imidazole with the Pc^{t}Fe μ-oxo dimer in hexane at 20°C, contains, according to elemental analysis, one imidazole molecule per phthalocyanine fragment. The position of the main band in the electronic absorption spectrum (λ_{max} 627 nm, which is unusual for monomeric phthalocyanines) and the slow (within 20 h) transformation into the bis-adduct suggest preservation of the dimeric structure with the Fe–O–Fe fragment in this intermediate; subsequently the presence of oxygen in similar complexes of type **D** was confirmed in [26, 51]. Proceeding from alternative structures **A** and **B** for the PcFe μ-oxo dimer, we should consider for complex **D** at least two possible structures: LPcFe(3+)–O–Fe(3+)PcL with axially coordinated base molecules and $(LH^+)_2[(PcFe)_2O]^{2-}$ {or $(H^+)_2[(LPcFe)_2O]^{2-}$ [43]} with outer-sphere cations and the iron oxidation state 2+. We prefer the second alternative, structure of the ionized dimer, in view of the following facts [35, 44]: The solubility of complex **D** in nonpolar solvents is considerably lower than that of the initial dimer; the electrolytic conductivity of the solvent abruptly increases immediately after adding the base, despite the fact that both the initial μ-oxo dimer and the bis-adduct are nonconducting; the position of the main absorption maximum in the electronic spectra of solutions of complexes **D** is independent of the ligand [L = Py, Im, piperidine (Pip), morpholine, quinoline, etc.], whereas for complexes $PcFe\cdot L_2$ [46, 47] such dependence exists (Table 1).

The latter fact indicates that the base L is not incorporated in the inner coordination sphere of the complex; therefore, we consider for solutions structure **D** as an ionized dimer with the protonated base LH^+ as counterion. As for the form of these complexes in the crystal, the structure $(H^+)_2[(LPcFe)_2O]^{2-}$ is the most consistent with the whole set of available physicochemical data. This problem is discussed in more detail in [43].

Table 1. Electronic absorption and Mössbauer data for complexes LcFe–L_2 at 77 K[a]

Complex {solvent with additions of L}[b]	λ_{max}, nm	δ,[c] mm s^{-1}	ΔE_Q, mm s^{-1}	References
$PcFe\cdot Pip_2$ {DMSO}	663	0.364	2.19	[46]
$PcFe\cdot Im_2$ {chloroform}	663	0.313	1.74	[46]
{DMSO}	656			[47]
$PcFe\cdot Py_2$ {chloroform}	655	0.322	1.94	[46]
{DMSO}	656			[47]
		0.31	2.04	[48]
		0.26^d	2.02^d	[49]
		$0.53^{d,e}$	1.96^d	[50]
		$0.53^{e,f}$	2.05^f	This work
$Pc^tFe\cdot Py_2$ {benzene}	657	$0.518^{d,e}$	2.03^d	This work
$PcFe\cdot(3\text{-}MePy)_2$ {chloroform}	655	0.321	1.87	[46]
$PcFe\cdot(4\text{-}MePy)_2$ {chloroform}	656	0.347	1.97	[46]
$PcFe\cdot(3\text{-}OHPy)_2$ {DMSO}	656	0.355	1.90	[46]
$PcFe\cdot(4\text{-}OHPy)_2$ {DMSO}	662	0.365	1.80	[46]
$PcFe\cdot(3\text{-}ClPy)_2$ {chloroform}	653	0.343	1.91	[46]
$PcFe\cdot(4\text{-}ClPy)_2$ {DMSO}	680	0.389	2.45	[46]

[a] Here and hereinafter: (λ_{max}) position of the main absorption band (in the indicated solvent); (δ) isomer shift; (ΔE_Q) quadrupole splitting. [b] For electronic absorption spectra. [c] Relative to Fe_{met}. [d] At 295 K. [e] Relative to sodium nitroprusside. [f] At 80 K.

In view of these data, the observed temperature dependence of the ^1H NMR spectrum of the Pc^{t}Fe μ-oxo dimer may be due to occurrence of prototropic equilibrium (3) with variation of the center of proton localization, namely, with proton transfer from the pyrrolenine nitrogen atoms to the outer sphere of the complex to form the ionized μ-oxo dimer, an analog of compound **D**:

$$[HPcFe(2+)]_2O \rightleftarrows (H^+)_2\{[PcFe(2+)]_2O\}^{2-}. \qquad (3)$$

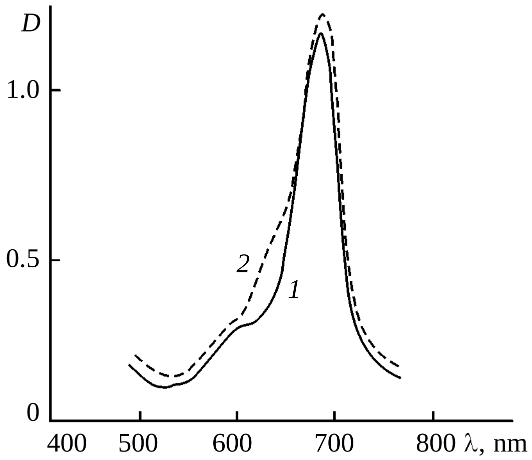

Fig. 1. Electronic absorption spectrum of iron tetra-4-*tert*-butylphthalocyanine μ-oxo dimer in toluene at (*1*) 295 and (*2*) 213 K.

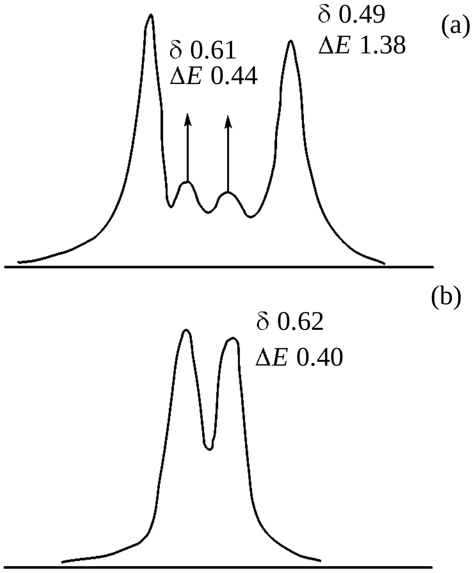

Fig. 2. Mössbauer spectra of iron tetra-4-*tert*-butylphthalocyanine μ-oxo dimer: (a) crystalline sample at 295 K and (b) frozen toluene solution at 80 K.

This assumption is confirmed by the fact that the electronic absorption spectrum of a toluene solution of the Pc^tFe μ-oxo dimer, recorded at –60°C (Fig. 1), contains a new shoulder at about 630 nm, which is close in position to that of the main absorption band in the spectrum of a solution of ionized μ-oxo dimer **D** (λ_{max} 627 nm) and belongs, apparently, to the complex $(H^+)_2\{[PcFe(2+)]_2O\}^{2-}$. Heating of the solution to room temperature completely restores the initial spectrum. Thus, the observed changes in the electronic absorption and ^1H NMR spectra are due to the shift of equilibrium (3) to the right with decreasing temperature. Comparison of the quantitative characteristics of the electronic absorption spectra of solutions of the initial Pc^tFe μ-oxo dimer and complex **D** formed from it allow the changes observed in the ^1H NMR spectrum on cooling and on adding pyridine to be explained as follows. The half-width (Δν) of the long-wave band reflects the efficiency of the electron exchange between the macrorings in the dimer. Judging from the measured values, in the ionized dimer $(PyH)_2^+[(Pc^tFe)_2O]^{2-}$ (Δν 2100 cm^{-1}) this electron exchange is more efficient in the initial Pc^tFe μ-oxo dimer (Δν 1730 cm^{-1}). This is probably due to the bent structure of the Fe–O–Fe fragment in the latter, in contrast to dimer **D** in which this fragment is practically linear [51, 52] (Fe–O–Fe angle 175.1° [52]); hence, the phthalocyanine rings are almost parallel, which increases the deshielding of the macroring protons and shifts their signals downfield. The same is apparently true for transition (3) from the Pc^tFe μ-oxo dimer to the "linear" structure of the ionized dimer $(H^+)_2\{[Pc^tFe(II)]_2O\}^{2-}$. The downfield shift of the macroring proton signals of the Pc^tFe μ-oxo dimer, in which there is noticeable electronic interaction between the phthalocyanine fragments, relative to the bis(pyridine) adduct Py_2Pc^tFe indirectly supports our reasoning.

The Mössbauer spectra recorded for several independent solid samples of the Pc^tFe μ-oxo dimer at 298 K (Table 2, Fig. 2) contain two doublets. The parameters of the major doublet (δ 0.41–0.49 mm s^{-1}, ΔE_Q 1.36–1.38 mm s^{-1}) are consistent with the oxidation state 2+ of the iron atom in this complex {e.g., the complex characterized by δ 0.23 mm s^{-1} and ΔE_Q 1.28–1.31 mm s^{-1} at 110 K is interpreted in [40] as a PcFe(2+) derivative; later, however, the same parameters were assigned [27] to one of the two isomeric crystalline forms of PcFe(3+)–O–Fe(3+)Pc, namely, to the so-called μ-oxo 2 form}. The parameters of the second, minor doublet (relative integral intensity ≤7%) suggest a more symmetrical environment of the iron ion as compared to the major form (δ 0.59–0.62 mm s^{-1}, ΔE_Q 0.40–0.44 mm s^{-1}). It should be noted that Kennedy *et al.* [34, 57] also observed two doublets with close parameters δ and ΔE_Q in the Mössbauer spectrum of unsubstituted PcFe μ-oxo dimer at 77 and 4.2 K (Table 2). However, in this case the internal doublet is the major component (and the sole component at room temperature). Following Frampton and Silver [40] [who, however, noted lower value of ΔE_Q as compared to iron(3+) porphyrin μ-oxo dimers], Kennedy *et al.* assigned this

Table 2. Mössbauer spectra of PcFe, its tetra-4-*tert*-butyl-substituted analog (Pc^{t}Fe), and the corresponding μ-oxo dimers[a]

Complex[b]	T, K	δ,[c] mm s^{-1}	ΔE_Q, mm s^{-1}	Relative content, %	References
PcFe	293	0.66[d]	2.64	–	[53]
	293	0.68[d]	2.67	–	[54]
	293	0.38	2.60	–	[55]
	81	0.64[d]	2.64	–	[53]
	77	0.45	2.62	–	[48]
	4.2	0.63[d]	2.62	–	[56]
Pc^{t}Fe	298	0.645[d]	2.614	–	This work
	77	0.686[d]	2.402	–	This work
(PcFe)$_2$O	295	0.25	0.42	–	[34, 57]
	77	0.36	0.44	90.8	
	77	0.25	1.35	9.2	
	4.2	0.37	0.44	87.3	
	4.2	0.24	1.38	12.7	
(PcFe)$_2$O	295	0.26	0.40	–	[27]
μ-oxo 1	110	0.34	0.38	–	[40]
	77	0.36	0.44	–	[34,57]
(PcFe)$_2$O	295	0.18	1.04	90.6	[27]
μ-oxo 2	295	0.25	0.42	9.4	[27]
	110	0.23	1.28–1.31	–	[27, 40]
	77	0.25	1.26	98.8	[27]
	77	0.32	0.35	1.2	[27]
(Pc^{t}Fe)$_2$O	82	0.22	1.39	93	[58]
	82	0.33	0.39	7	[58]
(HPc^{t}Fe)$_2$O – "a"	298	0.407[d]	1.362	~93	This work
	298	0.587[d]	0.444	≤7	This work
(HPc^{t}Fe)$_2$O – "b"					
Finely crystalline	298	0.491[d]	1.380	~93	This work
sample	298	0.616[d]	0.448	≤7	This work
In frozen toluene matrix	77	0.623[d]	0.403	100	This work

[a] The μ-oxo dimers are formulated as in original papers. [b] ("a", "b") Independent samples of (HPc^{t}Fe)$_2$O. [c] Relative to Fe$_{met}$. [d] Relative to sodium nitroprusside.

doublet to [PcFe(3+)]$_2$O. The external doublet was assigned in [34] to PcFe(OH$_2$)(OH) which was assumed to be formed by equilibrium reaction (4):

$$(PcFe)_2O \overset{H_2O}{\rightleftarrows} PcFe(OH) \overset{H_2O}{\rightleftarrows} PcFe(OH_2)(OH). \tag{4}$$

Our experiments showed that, in going from crystalline samples of the Pc^{t}Fe μ-oxo dimer to quickly frozen solutions in toluene, only the internal doublet remains in the Mössbauer spectrum (Fig. 2). Assuming occurrence of prototropic equilibrium (3) for the Pc^{t}Fe μ-oxo dimer, we should assign this doublet to the ionized dimer (H$^+$)$_2${[Pc^{t}Fe(2+)]$_2$O}$^{2-}$, since, as follows from the above-discussed ^{1}H NMR and electronic absorption spectra, this equilibrium shifts to the

Table 3. Mössbauer spectra of adducts of PcFe μ-oxo dimers with *N*-bases

N-Base	T, K	δ,[a] mm s^{-1}	ΔE_Q, mm s^{-1}	References
γ-Pic	4.2	0.46	1.79	[59]
4-MePy	4.2	0.46	1.76	[51]
Pip	4.2	0.45	1.61	[51]
1-MeIm	4.2	0.43	1.58	[51]
Py	4.2	0.44	1.73	[51]
Py[b]	80	0.43	1.73	This work

[a] Relative to sodium nitroprusside. [b] Adduct with the Pc^{t}Fe μ-oxo dimer.

right with decreasing temperature. As in the frozen toluene matrix the state of the Pc^{t}Fe μ-oxo dimer should correspond to its state in solution at the same temperature (77 K), it is quite probable that this dimer occurs practically exclusively in the form of the ionized dimer $(H^+)_2\{[Pc^tFe(2+)]_2O\}^{2-}$, which explains the presence of only one doublet in the spectrum. The parameters of this doublet are consistent with the assumed conformation of the PcFe(2+) μ-oxo dimer, because transfer of the proton to the outer coordination sphere makes the ligand environment of the iron ion more symmetrical than in the initial dimer **A**.

In view of structural similarity of the ionized dimeric complexes of iron phthalocyanine: complex **D** prepared from μ-oxo dimer A by the reaction with *N*-bases and the second complex formed by prototropic transformation (3), taking into account also the similarity of the electronic absorption and ^{1}H NMR spectra of these complexes in solution, it is logical to expect that the Mössbauer spectra of these compounds would also be similar. Unfortunately, the solubility of complex **D** in toluene is too low to record its Mössbauer spectrum. As for the spectrum of this complex in the solid state (Table 3), it is typical of compounds $(H^+)_2[(LPc^tFe)_2O]^{2-}$.

The Mössbauer parameters obtained by us for complex **D** practically coincide with those given in the literature for similar intermediates formed in the course of formation of bis-adducts of unsubstituted PcFe with various *N*-bases (Table 3). A striking feature is the similarity of the Mössbauer parameters for complexes **D** with different bases. In any case, the Mössbauer parameters of bis-adducts $PcFe(2+)\cdot L_2$ (Table 1) and of other adducts with *N*-bases, e.g., of porphyrin complexes LPFe(4+)=O [60, 61], are more strongly affected by the nature of axial ligands as compared to complexes **D**. This fact suggests larger distances between L and the coordination center (Fe atom) in complexes **D** as compared to bis-adducts. The X-ray diffraction analysis of the intermediate complex formed in the course of transformation of the unsubstituted PcFe μ-oxo dimer into its bis-adduct with 1-methylimidazole showed that the distance between Fe and the 1-MeIm nitrogen atom is 2.039 Å, being somewhat longer than the $Fe–N_{MeIm}$ bond in the bis-adduct (1.946 Å [52]). Note that the lack of significant differences in the Mössbauer parameters of complexes **D** and $PcFe\cdot L_2$ is an additional evidence of retention of the Fe oxidation state in the course of transformation of PcFe μ-oxo dimers into bis-adducts.

Let us now try to explain these experimental results from the viewpoint of alternative structure A of PcFe μ-oxo dimers. Ercolani *et al*. [24, 27] isolated and characterized the unsubstituted PcFe μ-oxo dimer in two “structurally isomeric” forms. They believe that form μ-oxo 1 has the bent structure with the Fe(3+) ions expelled from the macroring planes of the phthalocyanine fragments, and form μ-oxo 2 has a linear (or “quasilinear”) structure with the Fe(3+) ions in the macroring planes. The Mössbauer parameters (Table 2) reported for forms μ-oxo 1 (δ 0.36 mm s^{-1}, ΔE_Q 0.44 mm s^{-1} at 77 K) and μ-oxo 2 (δ 0.25 mm s^{-1}, ΔE_Q 1.26 mm s^{-1} at 77 K), are close to the values determined by us for the Pc^{t}Fe μ-oxo dimer and assigned to the ionized and un-ionized states of this complex {δ 0.59–0.62 mm s^{-1}, ΔE_Q 0.40–0.44 mm s^{-1} at 77 K for $(H^+)_2[(Pc^tFe)_2O]^{2-}$ and δ 0.49–0.59 mm s^{-1}, ΔE_Q 1.36–1.38 mm s^{-1} at 298 K for $(HPc^tFe)_2O$}. Note that, whereas until recently comparison of the isomer shifts and quadrupole splittings of various coordination derivatives of unsubstituted and tetra-4-*tert*-butyl-substituted PcFe was based on the fact that for PcFe and Pc^{t}Fe proper these parameters are close (Table 2), today the correctness of such comparison is further supported by data of Dieing *et al*. [58] who measured the Mössbauer spectra at 82 K of μ-oxo dimers of 12 different tetra- and octasubstituted PcFe with alkyl, alkoxy, and alkoxycarbonyl groups. These spectra consist of two doublets whose parameters are close to those determined by us for the Pc^{t}Fe μ-oxo dimer and reported in [27] for PcFe in the forms μ-oxo 1 and μ-oxo 2. Thus, the isomer shift and quadrupole splitting are practically insensitive to the electronic and steric properties of the peripheral substituents. These quantities vary in narrow ranges for all the R$_n$PcFe μ-oxo dimers studied in [58]: external doublet, δ 0.22 mm s^{-1}, ΔE_Q 1.33–1.39 mm s^{-1}; internal doublet, δ 0.33–0.36 mm s^{-1}, ΔE_Q 0.39–0.53 mm s^{-1}.

Assume that the spectral changes occurring on cooling of a solution of the Pc^{t}Fe μ-oxo dimer are due to the shift of equilibrium (5) between the two isomeric forms of this complex:

$$\mu\text{-oxo } 2 \rightleftarrows \mu\text{-oxo } 1. \qquad (5)$$

We emphasize that as the initial species we should undoubtedly consider μ-oxo 2, as specifically this isomer is similar in the Mössbauer parameters to the μ-oxo dimer studied spectroscopically by us. Then, the linear structure should transform into the bent structure with decreasing tempertature, and hence the ^{1}H NMR signals of the macroring protons should shift upfield owing to decrease in their deshielding. Our experiments with the Pc^{t}Fe μ-oxo dimer gave the opposite result.

When the Mössbauer spectrum of the Pc^{t}Fe μ-oxo dimer is recorded in a frozen toluene matrix, as noted above, the quadrupole splitting dramatically decreases as compared to the value measured for the crystalline sample at 298 K (ΔE_Q 0.40 and 1.36–1.38 mm s^{-1}, respectively). If, according to equilibrium (5), the linear structure with the symmetrical ligand surrounding of Fe transformed with decreasing temperature into the bent structure with the asymmetrical electronic environment of Fe, ΔE_Q, on the contrary, should increase.

Thus, the above-discussed ^{1}H NMR and Mössbauer data for the Pc^tFe μ-oxo dimer, considered separately or in combination, cannot be explained assuming the trivalent state of iron in the PcFe μ-oxo dimer and equilibrium (5) between the stereoisomeric species suggested by Ercolani *et al*. [24, 27]. As for the transformation of the electronic absorption spectrum of the Pc^tFe μ-oxo dimer in toluene, observed with decreasing temperature from 20 to –60°C, the spectra of the isomers μ-oxo 1 and μ-oxo 2 were not recorded at low temperatures, which does not allow any comparison. Let us dare to suggest that Ercolani *et al*. also dealt with the μ-oxo dimers similar to $[HPc^tFe(2+)]_2O$ and $(H^+)_2\{[Pc^tFe(2+)]_2O\}^{2-}$. Such suggestion, in any case, allows us to explain the fact, noted in [24], that not only the form μ-oxo 2 in chloronaphthalene in the presence of 2-propylamine can be transformed into the form μ-oxo 1, but also the form μ-oxo 2, vice versa, can be partially transformed into the form μ-oxo 1 by dissolution in *n*-butylamine followed by quick solvent evaporation. According to our concept, these transformations can be described by scheme (6).

$$\underset{\mu\text{-oxo 1}}{(H^+)_2[(PcFe)_2O]^{2-}} \underset{\substack{-L \\ (L\,=\,2\text{-}PrNH_2)}}{\overset{L}{\rightleftarrows}} (LH)_2^+[(PcFe)_2O]^{2-}$$

$$\underset{\substack{L \\ (L\,=\,n\text{-}BuNH_2)}}{\overset{-L}{\rightleftarrows}} \underset{\mu\text{-oxo 2}}{(HPcFe)_2O.} \qquad (6)$$

The identity of the electronic absorption spectra of the isomers μ-oxo 1 and μ-oxo 2, observed in the case of PcFe in such solvents are chloronaphthalene and chloroform and found for a large set of R_nPcFe in noncoordinating solvents [58], is due to the fact that these spectra presumably belong to the same compound, $(HPcFe)_2O$. The fact that the absorption spectra of solutions of μ-oxo 1 and μ-oxo 2 undergo similar transformations in pyridine and concentrated sulfuric acid [24, 27] is also consistent with this assumption.

Thus, the spectroscopic studies of the Pc^tFe μ-oxo dimer show that at low temperatures the protons are not fixed on the pyrrolenine nitrogen atoms, as might be expected, but are expelled into the outer sphere of the complex. This is probably due to the fact that in PcFe μ-oxo dimers the distortion of the inner coordination sphere is minimal when the proton migrates over four internal nitrogen atoms. If the proton is fixed on one of these atoms (which should occur at crystallization or with decreasing temperature), the distortion of the inner coordination sphere should increase, resulting in displacement of the proton to the outer sphere and restoration of the planar structure of the chelate core.

The whole set of data obtained by us in studying the Pc^tFe μ-oxo dimer prepared according to [33] and the published data for the μ-oxo dimers of unsubstituted PcFe [24–27, 34] and some of its substituted derivatives [11, 41, 42, 58] mainly support structure **B**, although some of these data are consistent with both alternative structures [43]. Structure **B** of the μ-oxo dimer as the PcFe(2+) coordination derivative can also be subject to criticism [36], in view of a very important fact: formation of the μ-oxo dimer directly from PcFe and O_2. If oxygen, as noted in [23, 25], actually reacts with PcFe in the molar ratio $O_2 : PcFe = 1 : 4$ to give the μ-oxo dimer as a sole product, this fact can hardly be explained assuming structure **B**. Formation of this structure requires a source of hydrogen atoms (reductant) in formation of $H_2[(PcFe)_2O]$ from PcFe and O_2.

With the aim to check published data, taking advantage of the high solubility of *tert*-butyl-substituted PcFe in noncoordinating solvents, we studied direct reaction of Pc^tFe with molecular oxygen in benzene.

The main quantitative results of experiments on the oxygen uptake with Pc^tFe solutions in benzene are listed in Table 4. However, before discussing the results, let us mention some methodical problems (see also Experimental). Since the experiments required large amounts of the proper tetra-4-*tert*-butyl-substituted analog of PcFe as the initial compound, we prepared this substance by vacuum heating of the bis(pyridine) adduct $Pc^tFe \cdot Py_2$. As compared to sublimation of the Pc^tFe μ-oxo dimer or bis(pyridine) adduct, this procedure provides higher yields of Pc^tFe (75–95 instead of 10–25%) but affords somewhat less pure samples. The main substance content in the samples was determined directly before the experiments by a specially developed and standardized procedure using the molar extinction coefficient of the acid complex $Pc^tFe \cdot HCl$ formed by Pc^tFe with HCl. As reference we used the value for analytically pure $Pc^tFe \cdot HCl$. This allowed us to calculate the absolute amount of Pc^tFe taken in an experiment and its initial concentration. The high solubility of iron tetra-4-*tert*-butylphthal-

Table 4. Quantitative data on the stoichiometry of reaction of the tetra-4-*tert*-butyl-substituted analog of iron phthalocyanine with molecular oxygen (T 18–22°C, P_{tot} 1.3–1.5 atm)

Run no.	Content of Pc^{t}Fe in sample, %	Amount of Pc^{t}Fe in experiment, a, mmol × 10^2	Initial concentration of Pc^{t}Fe, M × 10^2	Amount of O_2 taken up, mmol × 10^2	a/m	Amount of Pc^{t}Fe after experiment completion (in μ-oxo dimer), mmol × 10^2
1	94.9	53.82	0.63	10.77	5.00	50.85
2	92.0	52.94	1.06	12.46	4.25	50.76
3	93.0	51.29	2.05	15.23	3.37	44.40
4[a]	89.1	94.59	2.36	26.34	3.59	82.25
5[a]	93.0	94.95	2.37	28.12	3.38	88.04
6	94.6	54.18	2.71	12.98	4.17	52.41
7[a]	89.8	93.99	3.13	25.13	3.74	86.43
8	92.5	59.07	5.82	15.40	3.84	55.09
9	75.5	34.33	6.87	9.68	3.54	33.17
10	90.2	51.31	7.33	16.60	3.09	45.68
11	77.4	82.61	8.26	30.13	2.74	65.61
12	85.3	83.62	8.36	24.95	3.35	74.23
13	75.5	88.31	8.83	30.90	2.86	78.10
14	92.2	104.57	10.46	33.75	3.10	81.31
15	92.6	104.83	10.48	30.24	3.46	95.47
16[b]	92.7	53.10	10.62	17.39	3.05	44.32
17	91.5	107.06	10.71	36.16	2.96	96.09

Run no.	Consumption of Pc^{t}Fe in reaction with O_2, c		Content of Fe^{3+} ions in samples, %		Detected degradation products of Pc^{t}Fe, % of c	
	mmol × 10^2	% of a	before experiment	after experiment	irreversible	reversible
1	2.97	5.5	5.4	9.4	76.4	–
2	2.18	4.1	6.2	10.2	103.0	–
3	6.89	13.4	9.7	17.3	62.7	–
4[a]	12.34	13.1	5.2	10.3	43.9	–
5[a]	6.91	7.3	1.5	5.4	57.7	–
6	1.77	3.3	5.4	8.0	97.0	–
7[a]	7.56	8.0	1.2	5.7	62.9	–
8	3.98	6.7	6.2	11.1	78.0	–
9	1.16	3.4	–	–	–	27.0
10	5.63	11.0	9.7	16.7	70.7	25.8
11	17.00	20.6	–	–	–	15.0
12	9.39	11.2	9.3	13.7	45.9	52.0
13	10.21	11.6	–	–	–	17.0
14	23.26	22.3	6.2	14.4	40.0	58.0
15	9.36	8.9	9.2	17.2	96.5	–
16[b]	8.78	16.5	8.3	21.5	86.0	–
17	10.97	10.3	–	–	–	14.5

[a] The reaction was performed in cyclohexane (in other runs, in benzene). [b] Gas phase: 1 : 1 (v/v) mixture of O_2 and N_2; in other, runs air.

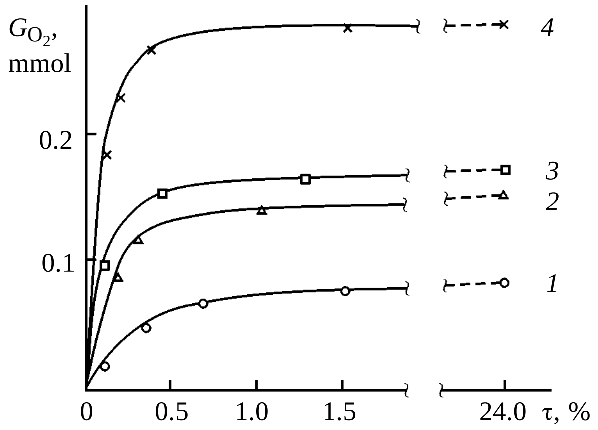

Fig. 3. Variation with time of the oxygen uptake with solution of Pc^tFe in benzene. $[Pc^tFe]_0 \times 10^2$, M: (*1*) 1.0, (*2*) 2.0, (*3*) 5.8, and (*4*) 10.0.

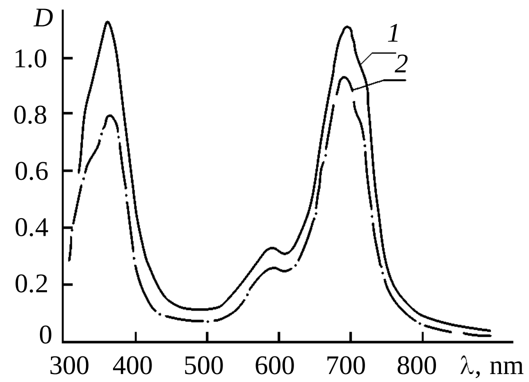

Fig. 4. Electronic absorption spectra of samples of series (*1*) K and (*2*) S of iron tetra-4-*tert*-butylphthalocyanine μ-oxo dimer in benzene solution ($[Pc^tFe]$ ~10^{-4} M).

ocyanine in benzene allowed us to perform experiments on the O_2 uptake in the range of initial concentrations of Pc^tFe from 6.3×10^{-3} to 1.071×10^{-1} M. Unfortunately, our procedure does not allow study of more dilute solutions, because at lower amounts of Pc^tFe taken in the reaction the volume of the oxygen taken up and hence the accuracy of its determination decrease. The possibility of increasing the solution volume is also limited. It should be emphasized that the reaction of unsubstituted PcFe with oxygen in DMF [23, 24] and DMSO [25], on the contrary, was studied at low PcFe concentrations [e.g., $(1-40) \times 10^{-5}$ M in the case of DMSO].

Experiments involving analysis of gas phase samples in the course of the reaction showed that Pc^tFe in benzene, in a wide range of initial concentrations, reacts with oxygen relatively fast: The major amount of oxygen is taken up within 1.5–2.0 h, and after approximately 1 day the uptake fully stops (Fig. 3). All subsequent experiments for determining the stoichiometry of the reaction of Pc^tFe with oxygen lasted for 1 day. The water content in the system $\{[H_2O]$ $(1.0 \pm 0.5) \times 10^{-2}$ M$\}$ before and after O_2 uptake remains practically unchanged. The spectrum of the reaction solution, diluted 40-fold with benzene, is typical of solutions of the Pc^tFe μ-oxo dimer, with the main absorption maximum at 690 nm; however, absorption in the range of the Soret band (λ_{max} 365 nm) is somewhat greater. Chromatography of this solution in a column with neutral alumina (eluent benzene) gives the individual Pc^tFe μ-oxo dimer in an yield of ~80% based on the loaded Pc^tFe.

The experimental results (Table 4) show that the molar ratio between the Pc^tFe taken in the reaction and O_2 taken up is not constant and depends on the initial concentration of the complex in the solution. In the studied range of Pc^tFe concentrations, this ratio varied from 5.0 to 2.7 and at $[Pc^tFe]_0 > 0.07$ M was appreciably less than 4. Analysis of these unexpected results revealed no correlation with the content of impurities in the Pc^tFe samples used. Thus, the stoichiometry of oxygen uptake determined for Pc^tFe significantly differs from that reported for unsubstituted PcFe [23–25].

After completion of oxygen uptake, benzene from the reaction solutions was evaporated at room temperature in a flow of dry nitrogen. The electronic absorption spectrum of the solid residue in benzene (Fig. 4) fully coincides with the above-described spectrum of the diluted reaction solution, recorded immediately after completion of the oxygen uptake. All the isolated samples were analyzed for the content of the Pc^tFe μ-oxo dimer (by ε of the complex with HCl), and most of them, also for the content of free Fe(3+) ions.

As seen from Table 4, the yield of the μ-oxo dimer based on the Pc^tFe taken in the reaction varies from ~97 to ~78%. In most of the experiments in which we detected free Fe(3+) ions in the solid residue after the reaction, their content amounts to only 40–86% of the loss of Pc^tFe in the side reactions with O_2. At the same time, in the initial samples the total content of Pc^tFe and Fe(3+) ions, determined by analysis, is always close to 100%. In some cases after completion of the O_2 uptake we detected in the gas phase over the reaction solution a small (~1%) amount of CO_2 (no more than 0.4 mol of CO_2 per mole of the lost phthalocyanine). Any other products of irreversible degradation of Pc^tFe, apart from Fe(3+) and CO_2, were not identified. These results suggest that irreversible oxidative degradation of PcFe, noted by us previously [62], is not the only factor responsible for the loss of Pc^tFe in the reaction with oxygen.

As one of the characteristics of the purity of Pc^tFe μ-oxo dimer samples obtained from the synthesis, we used the ratio α between the intensities of the main bands B (λ_{max} 365 nm) and Q (λ_{max} 690 nm) in the electronic absorption spectra of these compounds. For analytically pure samples of the Pc^tFe μ-oxo dimer, according to our data, $\alpha = D_{365}/D_{690} = 0.84 \pm 0.01$. Note that this value fully agrees with that recently reported in [63] for high-purity samples of Pc^tFe.

We found, however, that for solid samples isolated after oxygen uptake by Pc^tFe solutions α is always greater than 0.84 and varies within 0.93–1.12. It is known [64] that the products of reversible oxidation of the phthalocyanine macroring of the type $[Pc(X)_2Fe]$ exhibit absorption at about 360 nm. The overestimated values of α may be due to formation of such products, regenerating the chromophore under the action of reductants. To check the assumption that products of reversible oxidation are formed, we attempted in special experiments regeneration of the chromophore using as reductant ascorbic acid, as recommended in [64]. Regeneration was performed both with the reaction solutions after completion of oxygen uptake (Table 4, run nos. 9, 11, 13, 17) and with the isolated solid samples (run nos. 12, 14). We found that ascorbic acid, indeed, regenerates from 15 to 58% of the “decolorized” Pc^tFe. Note that in the experiments in which the products of both reversible and irreversible oxidation were determined quantitatively their sum is close to 100% (Table 4). After regeneration, the relative intensity of the absorption band with λ_{max} 365 nm decreases, and that of the band with λ_{max} 690 nm increases; correspondingly, α decreases to 0.86 – 0.89. These results show that reaction of Pc^tFe with oxygen is accompanied not only by irreversible oxidative degradation of the complex but also by reversible oxidation of the chromophore with addition of oxidant fragments to the α-C atoms to the pyrrole rings of the phthalocyanine [64]; in our particular case, OH groups add to give the complex $(HO)_2Pc^tFe$.

Unfortunately, we failed to reveal factors favoring reversible or irreversible oxidative transformations of Pc^tFe; it is only clear that the initial concentration of Pc^tFe in the reaction solution is not such a factor. Presumably, elevated temperatures favor irreversible degradation, since the Pc^tFe samples obtained from the bis(pyridine) adduct by heating to 493–503 K contain practically no products of reversible oxidation. It should be taken into account, however, that preparation of Pc^tFe from $Pc^tFe \cdot Py_2$ should be performed with precautions necessary to ensure practically total absence of oxygen in the system.

The most interesting result is the fact that a part of Pc^tFe in reaction with oxygen even under mild conditions undergoes oxidative (reversible and irreversible) degradation, which is beyond doubt. This important conclusion was confirmed by the fact that when the Pc^tFe μ-oxo dimer was prepared by the procedure in [33] but in an inert (Ar or N_2) atmosphere, the yield increased by more than 10%.

Thus, in reaction of the tetra-4-tert-butyl-substituted analog of iron phthalocyanine with oxygen in a benzene solution, the major reaction product is, indeed, the μ-oxo dimer, but its yield is significantly lower than 100%. The molar ratio of the Pc^tFe taken in the reaction and oxygen taken up depends on the initial concentration of the complex and at $[Pc^tFe]_0 > 7 \times 10^{-2}$ M is noticeably lower than 4 (the value obtained in [23–25] for unsubstituted PcFe).

Then, we made a comparative study of the samples of the Pc^tFe μ-oxo dimer prepared by simple evaporation of benzene in an inert gas flow after completion of the reaction of Pc^tFe with O_2 (hereinafter, samples K) and the purified samples obtained according to [33] (hereinafter, samples S). We compared their chemical behavior in reactions that are of principal importance for choosing between the two alternative structures **A** and **B** discussed for the iron phthalocyanine μ-oxo dimer.

A solution of samples K in benzene has a characteristic electronic absorption spectrum (Fig. 4) with the main absorption bands at 365 and 690 nm; the *Q* band is broad ($\Delta\nu_{1/2}$ 1730 cm^{-1}) is broad and has a more or less pronounced shoulder at λ 710 nm and a vibronic satellite at about 690 nm. This spectrum fully coincides with the spectra of the benzene solutions of samples S (Fig. 4) and resembles the published spectra of the μ-oxo dimers of unsubstituted PcFe [24, 30] and its substituted derivatives [10, 41, 42]. The higher intensity of the Soret band in the spectra of samples K compared to samples S was discussed above.

Here we again turned our attention to the common property of the μ-oxo dimers of both unsubstituted PcFe and its derivatives R_nPcFe, revealed in [30] and confirmed in the subsequent studies [10, 24, 27, 36]: reaction with nitrogen bases to give bis-adducts of the type $PcFe \cdot L_2$. As shown in [35, 44], transformation of samples S into such bis-adduct occurs via the intermediate dimeric ionized complex $(HL)_2^+[(Pc^tFe)_2O]^{2-}$ with λ_{max} 627 nm. An intermediate complex with such electronic absorption spectrum was also detected

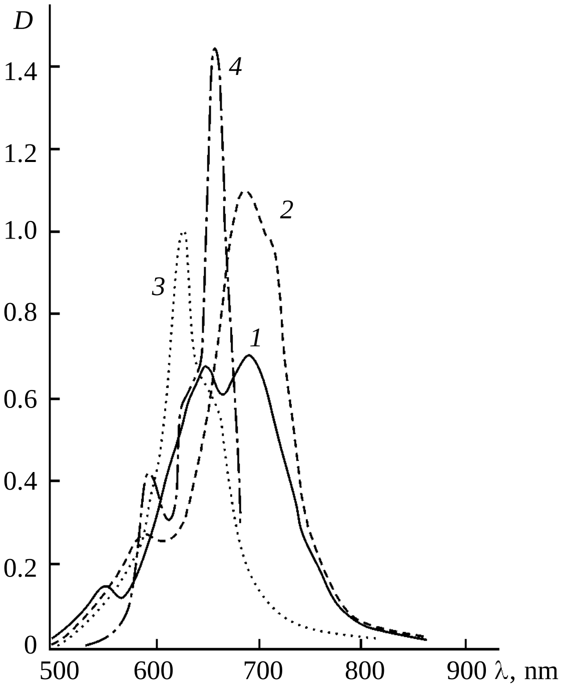

Fig. 5. Electronic absorption spectra recorded under anaerobic conditions at successive transformation of iron tetra-4-*tert*-butylphthalocyanine in benzene into the μ-oxo dimer and then via intermediate complex **D** into the bis-adduct with pyridine: (*1*) initial Pc^{t}Fe solution; (*2*) the same, after O_2 bubbling for 5 min followed by Ar bubbling for 30 min; (*3, 4*) reaction solution 5 min and 24 h, respectively, after adding pyridine.

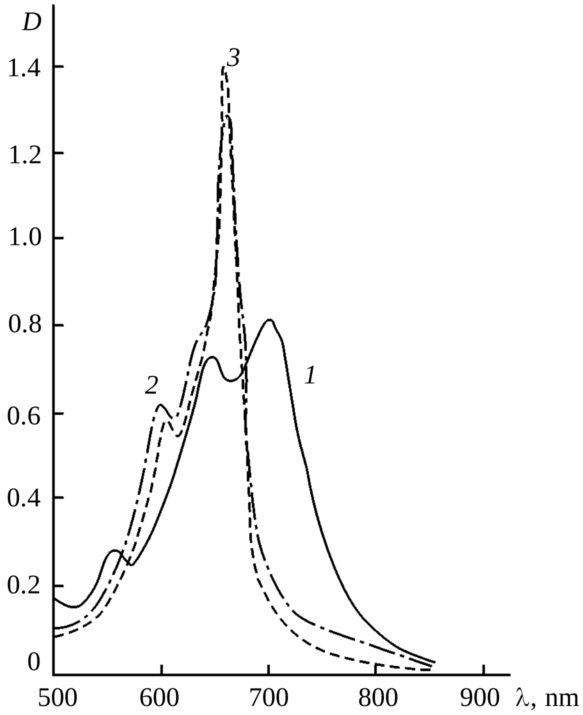

Fig. 6. Electronic absorption spectra recorded in the course of transformation of iron tetra-4-*tert*-butylphthalocyanine into the bis-adduct Pc^{t}Fe · Py_2 in benzene under anaerobic conditions at [Pc^{t}Fe]$_0$ ~10^{-3} and [Py] ~2.5 M: (*1*) before adding Py; (*2*) 5 min and (*3*) 24 h after adding Py.

by adherents of structure **A** in the course of transformation of $[(PcFe)_2O]$ into PcFe · L_2. However, those authors ascribe to this intermediate the structure of a nonionic complex, adduct of a base with the μ-oxo dimer molecule $[LPcFe(3+)]_2O$. However, when discussing the ^{1}H NMR spectra, we have already presented strong evidences in favor of the ionic structure of this complex with outer-sphere cations.

When oxygen is passed through a solution of Pc^{t}Fe in benzene, the μ-oxo dimer is rapidly formed (within 5–10 min), as judged from the spectrum (Fig. 5); after addition of Py it immediately transforms into intermediate complex **D** (λ_{max} 627 nm) and then into the bis(pyridine) adduct by scheme (2). The spectral pattern observed when benzene solutions of samples K are treated with pyridine or quinoline practically reproduces that given by curves 2–4 in Fig. 5 and that observed with samples S treated in benzene solution with Py, Im, quinoline, etc. [30, 35, 44]. It should be noted that the nature of the base affects only the position of the absorption maximum in the electronic spectra of the bis-adducts and the time required for complete conversion of the intermediate complex **D** into the final bis-adduct.

It is interesting that treatment of a benzene solution of Pc^{t}Fe with pyridine under strictly anaerobic conditions (flow of grade B helium additionally purified on the freshly regenerated catalyst of a standard PG device for gas deoxygenation) results in fast formation of Pc^{t}Fe · Pu_2, and no intermediate complexes are detected (Fig. 6).

Thus, in transformation into complexes of the type PcFe · L_2 samples S and K of the Pc^{t}Fe μ-oxo dimer exhibit similar behavior, differing from that of the initial Pc^{t}Fe in formation of the intermediate dimeric ionized complex $(HL)_2^+[(\mathrm{Pc}^t\mathrm{Fe})_2O]^{2-}$.

When studying the state in solutions of both unsubstituted iron phthalocyanine and its substituted analogs, the complexes PcFe · L_2, which have been known for a long time and reliably characterized [46, 65–71], can be used as references, because it is beyond doubt that these are the coordination derivatives of PcFe(2+). Hence, if the μ-oxo dimer has structure **A**, $[PcFe(3+)]_2O$, then its reaction with Py should be accompanied either by release of oxygen [reaction (7)] or by oxidation of pyridine, impurities in the solvent, or the solvent itself [reactions (8), (9)]:

$$2[(PcFe(3+)]_2O + 8Py \longrightarrow 4PcFe–Py_2 + O_2, \quad (7)$$

$$[(PcFe(3+)]_2O + 4Py + S \longrightarrow 2PcFe–Py_2 + SO, \quad (8)$$

$$[PcFe(3+)]_2O + 4Py + SH_2 \longrightarrow 2 PcFe–Py_2 + S + H_2O. \quad (9)$$

Here the reduced and oxidized forms of the solvent or impurities are conventionally designated as SH_2, S, and SO.

As reported in [36], in experiments on transformation of samples S of the μ-oxo dimer into the bis(pyridine) adduct, thorough analysis of the reaction solution and gas phase over it by GLC revealed neither oxygen nor possible products of pyridine oxidation (Py *N*-oxide; 4,4'- and 2,2'-bipyridines; 2-, 3-, and 4-hydroxypyridines). In similar experiments performed in this work with samples K we have not detected pyridine oxidation products and oxygen either. Volumetric measurements showed that the volume of the gas phase remained constant. The μ-oxo dimer of unsubstituted PcFe also transforms into the bis(pyridine) adduct without evolution of O_2. This fact was reliably established by Ercolani *et al.* [71] for the μ-oxo dimer and its ^{18}O-labeled sample by volumetry and mass spectrometry.

Thus, reaction (7) is rejected both by us and by adherents of structure **A**. Therefore, Ercolani *et al.* [71] suggested oxidation of impurities in the solvent, assuming that the resulting products could not be detected by common procedures because of their low content and unknown composition. To eliminate the uncertainty associated with reducing impurities [reactions (8), (9)], we added into the reaction system an a fortiori strong reductant and monitored formation of its oxidized form. As such reductant we used diphenylpicrylhydrazine whose oxidation product, diphenylpicrylhydrazyl (**II**), is readily detected in such solvents as benzene, nitrobenzene, or toluene by a strong absorption ($\varepsilon \sim 1.6 \times 10^4$ l mol^{-1} cm^{-1}) at λ_{max} 535 nm, i.e., in the range in which there are no absorption bands of any Pc^tFe species participating in the reaction. Experiments were performed in spectroscopic cells of a specially developed design with fittings for purging with gases and for sealing and with inserts allowing the layer thickness to be varied within 1.00–0.01 cm. Thus, it was possible to determine the content of diphenylpicrylhydrazyl in solution fairly accurately and to monitor the progress of transformation of the Pc^tFe μ-oxo dimer into the bis(pyridine) adduct at high initial concentrations of the starting complex. To avoid significant variation of reactant concentrations during purging with an inert gas, benzene in these experiments was replaced by the less volatile nitrobenzene. The concentration of pyridine was low but, as shown in independent experiments, sufficient for complete transformation of the initial complex into $Pc^tFe \cdot Py_2$ (as a rule, 4 or 8 mol of Py per mole of the μ-oxo dimer). If structure **A** is correct, 1 mol of the oxo dimer should oxidize 2 mol of diphenylpicrylhydrazine. Therefore, its concentration in the experiments exceeded that of the Pc^tFe μ-oxo dimer by a factor of at least 2.

The results of the experiments (Table 5) showed that, first, the Pc^tFe μ-oxo dimer in the absence of Py efficiently catalyzes oxidation of diphenylpicrylhydrazine. If the reaction system contains no oxygen, reaction of both samples S and K of Pc^tFe μ-oxo dimer with diphenylhydrazine in nitrobenzene results in formation of diphenylpicrylhydrazyl in an yield no more than 12% based on the μ-oxo dimer, which is apparently due to an O_2 impurity. Such extent of deaeration was attained by preliminarily passing helium, additionally deoxygenated on a freshly regenerated catalyst of a standard PG device for gas purification, for 2 h through the initial reaction solutions, by performing all manipulations (mixing of solutions) in a flow of this gas, and by subsequently sealing the cells. In the presence of even traces of O_2 formation of $Pc^tFe \cdot Py_2$ is accompanied by catalytic (as judged from the maximal yields of diphenylpicrylhydrazyl) oxidation of diphenylpicrylhydrazine. Thus, in experiments in which instead of helium we used argon without additional purification, the yield of diphenylpicrylhydrazyl was 18.2 ± 7.5% (average of 7 runs). In experiments performed with nitrogen, in which the O_2 content is higher than in argon, the yield of diphenylpicrylhydrazyl varied from 25 to 125% (average of 17 runs 41%). In experiments performed with air, the yield of diphenylpicrylhydrazyl was 90–175%. These results show that oxidation of diphenylpicrylhydrazine is terminated without reaching the stoichiometry if the concentration of oxygen in the system is less than that of the μ-oxo dimer, and with excess oxygen it goes until the initial dimer is completely converted into $Pc^tFe \cdot Py_2$ which exhibits no catalytic activity under the experimental conditions.

These complications probably were not taken into account by Ercolani *et al.* [71] who added triphenylphosphine when performing reaction of the PcFe μ-oxo dimer with Py under nitrogen and considered formation of triphenylphosphine oxide as an unambiguous evidence of occurrence of reaction (8). It can be assumed, however, that $O{=}PPh_3$ is formed by oxida-

Table 5. Oxidation of diphenylpycrylhydrazine in nitrobenzene in the presence of μ-oxobis[iron(+2) tetra-4-*tert*-butylphthalocyanine] (form 690)

Sample of form 690	Experimental conditions		Py : form 690 molar ratio	Concentration, M × 10^3			Yield of diphenylpicrylhydrazyl based on form 690, %
	time, h	gas phase		form 690	diphenylpicrylhydrazine	diphenylpicrylhydrazyl	
S	~30	Air	0	0.55	10.00	7.11	646.4
S	4.0	He	8	1.00	2.20	0.12	6.0
K	~20	He	8	0.90	2.02	0.08	4.4
S	2.0	He	8	0.70	3.01	0.05	3.6
S	1.5	He	8	0.60	9.00	0.12	10.0
S	1.5	He	8	0.50	8.04	0.12	12.0
S	~20	He	4	0.90	2.01	0.12	6.7
K	~20	He	4	1.10	2.60	0.18	8.2
S	~40	He	4	1.00	2.43	0.13	6.5
S	5.0	He	4	0.80	2.00	0.00	0.0
S	1.5	He	4	0.74	4.38	0.08	5.4
S	~40	He	2	1.00	2.39	0.18	9.0
S[a]	6.0	Ar	4	1.20	2.50	0.55	22.9
K[a]	~20	Ar	4	1.14	2.40	0.57	25.0
S[a]	5.0	N_2	4	0.55	2.20	0.78	70.9
S[a]	4.0	N_2	8	1.32	5.90	1.03	39.0
S	4.0	Air	8	1.00	2.18	1.80	90.0
K	~40	″	8	0.70	3.02	1.81	129.3
S	~50	″	8	0.60	9.57	2.10	175.0

[a] Typical examples from series of experiments under Ar and N_2.

tion of PPh_3 with residual oxygen (the procedure and extent of nitrogen purification are not given in [71]) and its enrichment with ^{18}O is due to isotope exchange. This assumption seems probable, as our experiments with diphenylpicrylhydrazine show that the mere fact of formation of oxidation products ($O{=}PPh_3$ or diphenylpicrylhydrazyl) and even their quantitative yield based on the initial dimer do not prove occurrence of reaction (8) if exhaustive removal of oxygen from the reaction system is not ensured.

Thus, it can be considered as a proved fact that reaction of the iron phthalocyanine μ-oxo dimer with Py is not described by Eq. (7); as for Eqs. (8) and (9), our results on oxidation of diphenylpicrylhydrazine apparently contradict data of Ercolani *et al.* [71]; hence, independent evidences are required to conclude about the stoichiometry of transformation of the PcFe μ-oxo dimer into the bis(pyridine) adduct. In terms of our concept about the structure of the μ-oxo dimer as a PcFe(2+) derivative, its reaction with Py should be accompanied by release of 1 mol of water per mole of the reacted dimer:

$$(HPc^{t}Fe)_2O + 4Py \longrightarrow 2Pc^{t}Fe\cdot Py_2 + H_2O. \quad (10)$$

The release of water in accord with the stoichiometry of Eq. (10) for samples S was proved by us previously [36] using a specially developed procedure of quantitative determination of the released water by direct GLC analysis of the reaction mixture in thoroughly dried quinoline which was preliminarily analyzed for water content (Py was replaced by quinoline because the latter is less hygroscopic). Using this procedure, we also tested two independently prepared samples K of the Pc^{t}Fe μ-oxo dimer. The absence of crystallization or coordinated water in these samples was proved by the absence of OH stretching bands in the range 2600–3600 cm^{-1}. The results of the experiments in quinoline are listed in Table 6. The content of iron phthalocyanine in solid samples of type K was determined by the molar extinction coefficient of the complex with HCl [9]. The amount of the dimer was calculated assuming that Pc^{t}Fe that had not underwent oxidative degradation in the course of preparation of samples K (reaction of Pc^{t}Fe with oxygen) quantitatively transformed into the μ-oxo dimer. Thus, in each experiment the number of moles of the μ-oxo dimer in the reaction with quinoline was 0.5 of the number of moles of Pc^{t}Fe. The latter value was determined from the weight of the sample and the results of the test

Table 6. Release of water in reaction of quinoline with μ-oxobis[iron(2+) tetra-4-*tert*-butylphthalocyanine] prepared by synthesis (samples S) and by reaction of Pc^{t}Fe with oxygen (samples K)

Sample	Content of Pc^{t}Fe in sample, %	Amount, mmol × 10^2			Yield of H_2O, %
		dimer in experiment	introduced PPh_3	released H_2O	
K	74.8	1.19	0.00	1.15	96.6
K	74.8	1.15	0.00	1.13	98.3
K	74.8	1.23	1.38	1.21	98.4
K	72.3	1.16	0.00	1.18	101.7
K	72.3	1.18	0.00	1.08	91.6
K	72.3	1.26	2.61	1.21	96.0
S	100	1.61	0.00	1.56	96.9
S	100	1.74	0.00	1.72	98.9
S	100	8.77	16.63	8.56	97.6

Table 7. Formation of water in reaction of iron(2+) tetra-4-*tert*-butylphthalocyanine in benzene successively with oxygen and quinoline

Amount of Pc^{t}Fe, mmol × 10^2	Maximum attainable yield of μ-oxo dimer,[a] mmol × 10^2	Time of reaction of Pc^{t}Fe in benzene with O_2, h	Amount of formed water, mmol × 10^2	Yield,[b] %
10.6	4.77	~0.02	0.30	6.3
11.2	5.04	~0.04	1.83	36.3
10.2	4.59	~0.04	1.60	34.9
10.9	4.91	0.33	1.41	28.7
9.8	4.41	0.75	3.33	75.5
10.4	4.68	0.75	3.27	70.1
11.2	5.04	1.00	4.37	86.7
10.0	4.50	~24.0	3.56	79.1
11.6	5.22	~24.0	5.02	96.2
10.1	4.54	~24.0	4.28	94.3
9.7	4.37	0.00	0.00	0.0

[a] In 24-h reaction of Pc^{t}Fe with O_2. [b] Based on the maximum possible amount of μ-oxo dimer.

with HCl. Experiments with samples S, included in Table 6, were performed in parallel to check the reproducibility of the experimental procedure [36] and directly compare the results obtained with samples of the Pc^{t}Fe μ-oxo dimer of different origins. The completeness of transformation of the initial complex into the bis(quinoline) adduct was checked by the electronic absorption spectra. The results show that the stoichiometry of Eq. (10) is followed fairly strictly, irrespective of the procedure used for preparing the samples. This fact rules out scheme (8) of oxidation of impurities S or reactants with formation of oxides or oxy derivatives.

However, Eq. (9) (oxidation of impurities of the type SH_2) is similar to reaction (10) in stoichiometry with respect to water. We have checked this possibility previously [36] for samples S and in this work for samples K by introducing triphenylphosphine as a competing reductant giving no water. The concentration of PPh_3 in solutions was comparable with that of the Pc^{t}Fe μ-oxo dimer and a fortiori higher than that of impurities (Table 6). If, as suggested in [52], the μ-oxo dimer $[PcFe(3+)]_2O$ were indeed the source of oxygen in triphenylphosphine oxide, PPh_3 competing with SH_2 would noticeably decrease the amount of water formed in reaction of the Pc^{t}Fe μ-oxo dimer with quinoline or fully prevent its formation. However, data in Table 6 and previous experiments with samples S [36] show that addition of PPh_3 does not decrease the yield of water per mole of reacted dimer, irrespective of the procedure used for preparing the dimer. These data and the above-considered data on oxidation of diphenylpicrylhydrazine, apparently, effectively rule out the hypothesis implying oxidation of substrates of the type SH_2.

Nevertheless, water released in the above experiments from the μ-oxo dimers of type K originates from the oxygen taken up. This is indicated by experiments on reaction with quinoline of benzene solutions of Pc^tFe after uptake of different amounts of oxygen. A weighed portion of Pc^tFe was dissolved in benzene in a vessel equipped with a device for sealing under strictly anaerobic conditions. The resulting solution was contacted with dry O_2 for a period varying from ~1 min to 24 h, i.e., the contact time in some experiments was sufficient for the reaction of Pc^tFe with O_2 in benzene to go to completion. Then the solution was quickly frozen, and the vessel was purged with thoroughly dried and deoxygenated argon, sealed, and thawed. This procedure was repeated no less than five times, after which deoxygenated quinoline was added in an inert atmosphere. In parallel, a blank experiment was performed in a similar vessel, with all the same manipulations including addition of quinoline but without Pc^tFe. After formation of the bis(quinoline) adduct of Pc^tFe was complete, the amount of the released water was determined as the difference between its content in the reaction solution with the Pc^tFe complex and in the benzene–quinoline mixture from the blank experiment. The results of these experiments are listed in Table 7. The weighed portion of Pc^tFe was corrected for the main substance content in the sample, determined directly before use from the absorption of its complex with HCl. The amount of the dimer that should be formed upon uptake of the maximum possible volume of oxygen was calculated assuming 10% loss of Pc^tFe for oxidative degradation, based on our data (Table 4). Correspondingly, the yield of water was calculated with respect to the stoichiometric amount that should be released under the action of quinoline [reaction (10)] on the Pc^tFe μ-oxo dimer in the amount determined as described above.

Our results show that the amount of water released in the subsequent reaction with quinoline varies in parallel with the time of reaction of Pc^tFe benzene solutions with O_2. In a control experiment in which the Pc^tFe solution did not contact O_2 and was kept for 24 h under dry oxygen-free argon, the amount of water in the reaction solution after formation of the bis(quinoline) adduct was the same as in the blank experiment. Figure 7 demonstrates the influence of the time of contact with oxygen of Pc^tFe in benzene on the amount of O_2 taken up (curve *1*), expressed in percents of the maximum possible oxygen uptake (in 24 h), and on the yield of water (curve *2*) in the subsequent reaction with quinoline. Data required for experiments on reaction of Pc^tFe with oxygen in benzene. Thus, the longer the contact of the Pc^tFe solution with O_2, the larger the uptake of oxygen and the higher the yield of H_2O in the subsequent formation of $Pc^tFe \cdot L_2$ by reaction with quinoline. This trend shows that the water determined in the reaction products does not have external origin and is formed by successive reactions of Pc^tFe with oxygen and of the resulting μ-oxo dimer with quinoline.

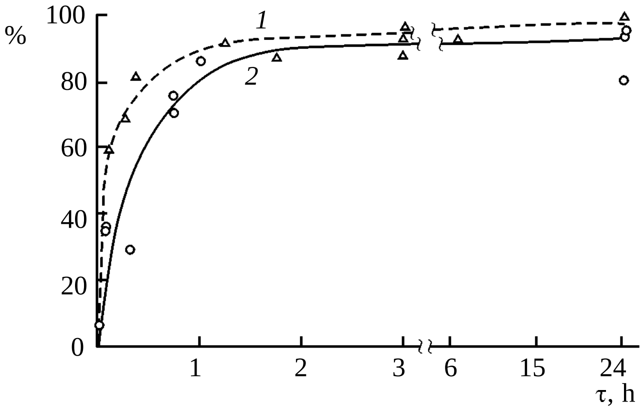

Fig. 7. Influence of the time of contact with oxygen of Pc^tFe in benzene (*1*) on the amount of O_2 taken up, expressed in percents of the maximum possible oxygen uptake, and (*2*) on the yield of water in the subsequent reaction with quinoline, based on the maximum possible amount of the μ-oxo dimer that should be formed in 24-h reaction with oxygen from the taken Pc^tFe.

Thus, the behavior of samples S and K in several principally important reactions not only confirms the fact that both these compounds (isolated from the synthesis and prepared by reaction of Pc^tFe proper with oxygen in a noncoordinating solvent) are the same Pc^tFe μ-oxo dimer and supports our identification of the μ-oxo dimer as a PcFe(2+) coordination derivative, $H_2[(PcFe)_2O]$. Note that recently Heucher *et al.* [72] arrived at the same conclusion on the structure of the Pc^tFe μ-oxo dimer. The whole set of data on reaction of Pc^tFe with O_2 in benzene suggest that the oxygen taken up is spent for oxidation of Fe(2+), phthalocyanine macroring, substituents in it, and, possibly, some other substrate, which was not identified in published papers and in our experiments; one of the oxidation products is water. Although the μ-oxo dimer is formed by reaction of Pc^tFe with water rather than directly with oxygen, consumption of water for its formation is compensated by its release in oxidation processes. The possibility of direct reaction of

Pc^tFe with water in dilute solutions ($C_{Pc^tFe} < 1 \times 10^{-3}$ M) to give the μ-oxo dimer (though with a very low rate) was noted by us in [73]. Traces of oxygen accelerate this reaction. It is quite probable that all these processes occur via a common intermediate complex of Pc^tFe with O_2 as shown in scheme (11):

$$2Pc^tFe + 2O_2 \longrightarrow 2[Pc^tFeO_2]$$

$$\begin{aligned} &\longrightarrow 2Fe(3+) + CO_2 + ? + (H_2O\ ?,\ H_2O_2\ ?), \\ &\xrightarrow{4SH_2} 2Pc^tFe + 4S + 4H_2O, \\ &\xrightarrow{2H_2O} 2(HO)_2Pc^tFe + O_2, \\ &\xrightarrow{H_2O} H_2[(Pc^tFe)_2O] + 2O_2. \end{aligned} \qquad (11)$$

As the amount of Pc^tFe that irreversibly degraded in the reaction with O_2 and the amount of CO_2 detected in the reaction products, even in total, are low as compared to the amount of the forming μ-oxo dimer, we attempted to find another source of hydrogen atoms incorporated, according to our concept, into the structure of the complex. Oxidation of benzene usually used as solvent in our experiments should yield diphenyl. However, GLC analysis of the reaction mixture revealed no diphenyl. Furthermore, check weighing of Pc^tFe before the experiment and of the solid product isolated after O_2 uptake revealed no weight gain other than that due to the O_2 uptake. Then we performed experiments on oxygen uptake with Pc^tFe in cyclohexane which is more reactive than benzene toward oxidation. In Table 4 we included data of those experiments in which, along with search for the possible products of cyclohexane oxidation, we also performed the majority of “standard” analyses made when studying the reaction of Pc^tFe with O_2 in benzene. The results showed that the use of cyclohexane solvent instead of benzene brings about no significant changes in the reaction stoichiometry. In this case the GLC analysis of the reaction mixture also revealed no products of solvent oxidation (cyclohexanone, cyclohexanol). Tests for the presence of cyclohexene (bromination, sensitivity 5×10^{-3} M), performed both with the reaction solution and with the solvent distilled off after the oxygen uptake, also gave negative results. Thus, the potential internal sources of protons in the course of formation of the μ-oxo dimer from Pc^tFe and O_2, found by now, are oxidation of Fe(2+) to Fe(3+) and irreversible oxidative degradation of the phthalocyanine macroring and, possibly, substituents.

Thus, reaction of tetra-4-*tert*-butyl-substituted iron phthalocyanine with O_2 yields the μ-oxo dimer indiscernible in the composition and properties from the previously described product of the synthesis from the corresponding phthalodinitrile and iron compounds. The qualitative and quantitative study of the reaction of Pc^tFe with O_2 showed that oxygen is spent not only for formation of the μ-oxo dimer but also for oxidative degradation of the macroring. The latter reaction may be the source of protons required for formation of the dimer $(HPcFe)_2O$. The whole set of previously described physicochemical and chemical properties of PcFe μ-oxo dimers, supplemented by the studies of the Pc^tFe μ-oxo dimer by ^1H NMR, Mössbauer, and electronic absorption spectroscopy at variable temperature, made in this work, support our assumption that this compound is an Fe(2+) complex.

EXPERIMENTAL

Chemically pure or analytically pure grade benzene was treated to remove thiophene according to [74], dried over neutral alumina, and fractionated. Chemically pure grade pyridine was distilled from KOH. Pure grade quinoline was dried over KOH and vacuum-distilled (5 mm). The fraction collected at 378 K was additionally dried in a column with freshly calcined alumina in a flow of dry nitrogen. Diphenylpicrylhydrazine was purified by reprecipitation from benzene with hexane and dried in a vacuum desiccator (10^{-2} mm) for 2 h. Gaseous helium (B grade), argon, and nitrogen were dried and deoxygenated with a standard PG gas purification device. If required, gases were also dried by freezing out moisture (Ar, O_2, and air at 193–213 K; He at ~80 K).

When manipulations were performed in an inert atmosphere, gas from the PG device was distributed using a manifold with Teflon capillaries. The glassware and equipment were purged with an inert gas directly before use. Solvents were deaerated by prolonged (up to 2 h) purging with an inert gas and transferred with pipets, which were also equipped with Teflon capillaries and purged with an inert gas.

The procedure for preparing μ-oxobis(iron *N*-hydrotetra-4-*tert*-butylphthalocyanine) (Pc^tFe μ-oxo dimer, form 690) was described previously [33].

Iron tetra-4-*tert*-butylphthalocyanine bis(pyridine) adduct ($Pc^tFe \cdot Py_2$). All manipulations were performed in an inert atmosphere. An analytically pure sample of the Pc^tFe μ-oxo dimer (~0.75 mmol) in ~0.87 mol of pyridine was stirred at 353–358 K for 1.5–2 h, after which excess pyridine was quickly distilled off in a vigorous argon flow. The resulting solid sample was dissolved in benzene–pyridine (30 vol %) and chromatographed in a column packed with alumina with the same solvent system as eluent. The solvent was removed to dryness in a vigorous argon flow under reduced pressure (P_{resid} ~10^2 mm) at room temperature. The resulting solid was dried in a desiccator over silica gel and filter paper impregnated with paraffin for 2–3 days. Found, %: C 73.57, 73.26; H 6.36, 6.30; N 15.20. $C_{58}H_{58}FeN_{10}$. Calculated, %: C 73.25; H 6.15; N 14.73.

Iron tetra-4-*tert*-butylphthalocyanine (Pc^tFe). All manipulations were performed in an He flow. Pc^tFe was prepared by heating analytically pure samples of $Pc^tFe \cdot Py_2$ in a vacuum (P_{resid} 0–1 mm) with continuously feeding He through a glass capillary. The ampule with a $Pc^tFe \cdot Py_2$ sample (0.9–1.5 g) before heating was evacuated to P_{resid} 0–1 mm, after which the gas flow rate through the capillary was increased, the pressure in the ampule was raised to 250–300 mm, and the ampule was again evacuated. This treatment was repeated 8–10 times at room temperature and then 9–10 times at 333–353 K. After that, the ampule was quickly heated to 498 ± 5 K and kept at this temperature for 2 h. The resulting Pc^tFe samples were kept in sealed ampules in an He or Ar atmosphere.

Procedures for determining the content of Pc^tFe and Fe(3+) ions in samples of Pc^tFe and its μ-oxo dimer. All manipulations except spectrophotometric measurements were performed in an inert atmosphere (Ar or He).

To determine the content of Pc^tFe, a sample of the substance (1.7–2.0 mg) was placed in a 25 cm^3 volumetric flask, and 15 ml of benzene and 3 ml of 1% aqueous HCl were added. The flask was treated in an ultrasonic bath for 30 min and left for 2.0–2.5 h for phase separation. The aqueous layer was discarded, and the benzene layer was brought to the mark with benzene and mixed. The optical density of the resulting solution was measured at λ 656 nm (l 0.01 cm), and the molar extinction coefficient ε of the complex $Pc^tFe \cdot HCl$ was calculated. The content of Pc^tFe was calculated from the ratio of ε of the complex prepared by reaction of the test sample with HCl to ε of analytically pure $Pc^tFe \cdot HCl$ [9].

To determine the content of free Fe(3+) ions, a sample (4.5–6.5 mg) of the complex was placed in a 50 cm^3 volumetric flask, and 15 ml of benzene and 10 ml of 1% aqueous HCl were added. The flask was treated in an ultrasonic bath for 30 min and left for ~2 h for phase separation. The aqueous layer was separated, and from the benzene layer the Fe(3+) ions were stripped with 5 ml of 1% aqueous HCl. Then, 2-ml samples of aqueous extracts were taken, 1 ml of 1 M aqueous NH_4SCN was added to each of them, the samples were mixed, and their optical density at λ 460 nm (l 1 cm) was measured. The concentration of free Fe(3+) ions was determined using the calibration chart, and their content in the sample was calculated.

Reaction of Pc^tFe with oxygen. Experiments on reaction of Pc^tFe with O_2 were performed in thick-walled narrow-necked flasks with an attachment allowing evacuation and sealing of the vessel, purging, gas feeding, and sampling of the gas phase. The Pc^tFe sample weight and the volume of the flask and benzene were varied depending on the desired concentration of Pc^tFe, so that at P_{tot} ~1140 mm the initial ratio of Pc^tFe and oxygen be approximately the same in all experiments. Typical procedure. Into a 55 cm^3 flask purged with argon, in an argon flow, 10 ml of deaerated benzene was added with a pipet equipped with a thin Teflon capillary and preliminarily purged with Ar. The flask was sealed, and the content was frozen at ~243 K. Then the flask was opened wihtout withdrawal from the cooling bath, and a ~0.5–1.0-g sample of Pc^tFe weighed with an accuracy of 0.01 mg was added in an Ar flow. The sample was deaerated in a weak Ar flow for ~30 min. Then the flask was evacuated and sealed, and 68 cm^3 of dry air was injected with a syringe. The solvent was thawed, and Pc^tFe was completely dissolved with stirring. In the course of contact of the Pc^tFe benzene solution with O_2, 0.1 cm^3 samples of the gas phase were taken at regular intervals and analyzed by GLC. The oxygen uptake by time τ was calculated by the formula

$$X_\tau = (K_2 - K_\tau)\,\frac{V_0(p_0^{O_2} + p_0^{N_2})}{K_1 + 1}\,\frac{V_f - V_b(1 - q_{O_2})}{V_f - V_b(1 - q_{N_2})},$$

where $K_1 = p_0^{O_2}/p_0^{N_2}$ is the ratio of the partial pressures of O_2 and N_2 in the initial gas mixture; $K_2 = K_1[V_f - V_b(1 - q_{N_2})]/[V_f - V_b(1 - q_{O_2})]$; $K_\tau = p_\tau^{O_2}/p_\tau^{N_2}$ is the ratio of the partial pressures of O_2 and N_2 in the gas mixture by time τ; V_f is the flask volume, cm^3; V_b is the volume of benzene added, cm^3; V_0 is the volume of the gas mixture injected, cm^3; q_{O_2} and q_{N_2} are the solubilities of oxygen and nitrogen in benzene, cm^3/cm^3.

This formula is valid if $P(n - 1)/(1 + m_{N_2}) << 1$, where n is the ordinal number of the gas sample; P is the volume ratio of one (and each) gas sample to V_0; m_{N_2} is the volume ratio of nitrogen dissolved in benzene to nitrogen in the gas phase before taking nth sample.

The GLC analysis was performed with a Tsvet-100 chromatograph. Conditions for analysis of gaseous substances (O_2, N_2, CO): thermal conductivity detector, 5 Å molecular sieves, 0.25–0.50-mm fraction, 3000 × 3-mm column, column and injector temperature 50°C, detector temperature 80°C, carrier gas Ar. Conditions for determination of water in the liquid phase: thermal conductivity detector; Porapak Q;

2000 × 3-mm column; temperatures, °C: column 230, injector 260, and detector 250; carrier gas He. Conditions for analysis of expected products of pyridine oxidation (pyridine *N*-oxide, 2,2'- and 4,4'-bipyridine, hydroxypyridines, 3-hydroxypyridine *N*-oxide): thermal conductivity detector; 15% Apiezon H on Chromaton N-AW, 0.250–0.315-mm fraction; 2000 × 3-mm column; temperatures, °C: column 190, injector 330, and detector 250; carrier gas He. Conditions for analysis of expected products of cyclohexane oxidation: flame-ionization detector; carrier gas He, flow rate 30 ml min^{-1}; 5% XE-60 on Chromaton N-AW, 0.160–0.200-mm fraction; 2000 × 3-mm column; temperatures, °C: column 180 and injector 210.

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