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CHEMICAL KINETICS AND CATALYSIS

Kinetics of the Chemical Oxidation of (5,10,15,20-Tetraphenyl-21H,23H-porphinato)(chloro)(aqua)iridium(III)

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Abstract—The oxidation of (Cl)(H_2O)IrTPP with atmospheric oxygen in the presence of concentrated H_2SO_4 accompanied by coordination of molecular O_2 and substitution of axial ligands was studied spectrophotometrically. In 16.785–18.09 M H_2SO_4 at 298–318 K, (Cl)(H_2O)IrTPP experienced two single-electron oxidations in sequence: with an increase in the oxidation state of the iridium cation and with formation of the π-radical cation form $(HSO_4)Ir^{IV}TPP^{\bullet +}$ oxidized at the aromatic ligand ($k^{298} = 7.2 \times 10^{-6}$ mol^{-1} L s^{-1}). Referring to the literature data on the oxidation of (Cl)(H_2O)IrTPP in AcOH and CF_3COOH, it was shown that the medium acidity and the nature of the axial ligands affect the electron removal site in the chemical oxidation of (Cl)(H_2O)IrTPP with atmospheric oxygen in proton-donor solvents.

Keywords: meso-tetraphenylporphin, iridium, complexes, π-radical cations, chemical oxidation, kinetics.

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INTRODUCTION

Interest in iridium compounds has rapidly increased in recent years. Of particular interest are porphyrin complexes denoted as $(X)_{n-2}$(L)IrP in the majority of publications (this contradicts the IUPAC notation, but is convenient because of the axial and equatorial ligands are indicated separately: X is the singly charged anion, L is the molecular ligand, and P is the porphyrin dication). These complexes have interesting photophysical [1, 2] and catalytic [3–8] properties directly related to the presence or absence of axial ligands in the fifth and sixth coordination sites of hexacoordinated porphyrin complexes. Thus, the molecular carbonyl CO ligands, which are generally present in (porphyrinato)iridium(III), do not favor the catalytic activity of the complexes, and there are few examples of catalysis involving $(X)Ir^{III}P$ compared with similar pentacoordinated rhodium(III) compounds with a vacant axial position.

The role of axial ions (molecules) or vacant coordination sites in the chemical reactivity, which is often comparable to the role of the coordinated macrocycle, was shown, at a quantitative level, on numerous examples of porphyrin complexes with metal ions (MP) [9–14]. In case of oxidation of MP in acids, we probably deal with processes involving molecular oxygen [15] similar to the processes studied for simpler (not macrocyclic) complexes of the metals of the cobalt subgroup [16]. In this case, as well as in reactions of MP-catalyzed oxidations in aqueous organic solvents [17–19], the products or intermediates are radical cations with a delocalized unpaired electron in the aromatic system of the macrocycle. As it is known [20], the $MP^{+\bullet}$ π-radical cations are stable in the medium of their formation and even after isolation into neutral solvents. They have some specific properties, in particular, spectral properties, according to which they can readily be recognized.

Based on the presented material, the $Ir^{III}P$ modification is evidently promising, according to the axial coordination sites and their stable redox forms, for substantiating the mechanisms and choosing the best conditions of catalysis on MP. This paper presents the synthesis and data for identification of (5,10,15,20-tetraphenylporphyrinato)(chloro)(aqua)iridium(III) (Cl)(H_2O)Ir^{III}TPP and the results of a kinetic study of the reactions of the complex in aqueous H_2SO_4 with different compositions. Using previously obtained data [21] on similar transformations of (Cl)(H_2O)Ir^{III}TPP in 99% CF_3COOH, we determined the effect of modification of the axial coordination sites in the molecules in solution on the physicochemical properties and reactivity of $Ir^{III}P$.

EXPERIMENTAL

(5,10,15,20-Tetraphenylporphinato)(chloro)(aqua) iridium(III) (Cl)(H_2O)Ir^{III}TPP and (hydroxo) (5,10,15,20-tetraphenylporhinato)(aqua)iridium(III) (OH)(H_2O)Ir^{III}TPP. A 9 : 1 mixture of the complexes was obtained from H_2TPP and $(H_3O)_2IrCl_6$ in a molar ratio of 1 : 5 in boiling phenol and purified by the procedure of [22]. Then the mixture was cooled and dissolved in chloroform. The resulting solution was washed from phenol with water, concentrated, and chromatographed on alumina (Brockmann II grade) using chloroform. The iridium(III) complexes were found in the third zone of the chromatogram. The chloroform solution of the substance of the first zone contained $[IrCl(H_2O)_2]_2H_2TPP$, a donor–acceptor SAT complex of nonionized porphyrin H_2TPP and iridium(I) salt [22]; in the second zone, it contained an impurity with an indefinite composition. The solution of the compounds from the third zone was chromatographed for the second time on alumina using at first chloroform and then a benzene–$CHCl_3$ mixture. The solvent was distilled off, and the solid product dried in air. Yield 40%. UV–Vis spectrum (chloroform), λ_{max}, nm (logε): 395 (shoulder 3.91), 418 (5.78), 476 (shoulder 3.60), 508 (shoulder 3.73), 549 (4.42), 588 (3.81), 640 (3.63). ^{1}H NMR, $CDCl_3$, δ, ppm: $(Cl)(H_2O)$IrTPP. 9.06 (s, $8H_\beta$), 8.17 (d, $8H_o$), 7.75 (m, $12H_{m,p}$), 2.18 (s, 2H H_2O). $(OH)(H_2O)$IrTPP. 8.9 (s, $8H_\beta$), 8.58 (d, $8H_o$), 7.52 (t, $8H_m$), 7.36 (t, $4H_p$), 0.35 (s, 2H H_2O), −1.41 (s, 1H OH).

(5,10,15,20-Tetraphenylporphinato)(chloro)(acetic acid)iridium(III) $(Cl)(CH_3COOH)$IrTPP, (5,10,15,20-tetraphenylporphinato)chloro(ethanol)iridium(III) (Cl)(EtOH)IrTPP, and (hydroxo)(5,10,15,20-tetraphenylporphynato)(ethanol)iridium(III)(OH)(EtOH) IrTPP. A 3 : 1 : 1 mixture of complexes was obtained and purified by a similar procedure using C_2H_5OH–1% CH_3COOH instead of the benzene–$CHCl_3$ mixture in the second chromatography. IR, solid chaotic layer, ν, cm^{-1}: 465 and 526 ν_{as}(Ir–N), skeletal vibrations of the macrocycle and ν_s(Ir–N), skeletal vibrations of the macrocycle; 573 and 662 ν_{as}(Ir–O) and ν_s(Ir–O); 702 med., 754 s. γ(C–H) of the benzene ring; 802 s. γ(C–H) of the pyrrole ring, N–H; 1012 s. δ(C–H) of the pyrrole ring; 1045, 1072 med., 1207 s. δ(C–H) of the benzene ring; 1277 ν(C–N); 1320 ν(C=N); 1351 δ(O–H); 1441 med. skeletal vibrations of the pyrrole ring; 1488, 1597 med., 1622 ν(C=C) of the benzene ring; 2853 med., 2924 s. ν(C–H) of the pyrrole ring; 3026, 3054 ν(C–H) of the benzene ring. ^{1}H NMR, $CDCl_3$, δ, ppm: $(Cl)(CH_3COOH)$IrTPP. 9.06 (s, $8H_\beta$), 8.58 (d, $8H_o$, $J = 7.3$), 7.75 (m, $12H_{m,p}$), 1.78 (d, 3H, CH_3, $J = 7.3$). (Cl)(EtOH)IrTPP. 9.02 (s, $8H_\beta$), 8.1 (d, $8H_o$, $J = 7.3$), 7.75 (m, $12H_{m,p}$), 3.53 (m, 2H, CH_2). (OH)(EtOH)IrTPP. 9.09 (s, $8H_\beta$), 8.22 (d, $8H_o$, $J = 7.3$), 7.75 (m, $12H_{m,p}$), 3.63 (m, 2H, CH_2), −1.2 (s, 1H OH).

The UV–Vis, IR, and ^{1}H NMR spectra were recorded on an Agilent 8453 UV–Vis spectrophotometer, VERTEX 80v spectrometer, and AVANCE-500 spectrometer (Bruker, Germany, TMS internal standard), respectively. The solid layers of the complexes were formed for an IR spectral study by evaporating the $CHCl_3$ solvent from the solution of the complex on a silicon plate.

The decrease in the concentration of the substances in the kinetic experiments was controlled spectrophotometrically. The measurements were conducted in the cells with a thickness of 1 cm placed in a special thermostatted chamber in the cell compartment of the spectrophotometer. The error in determining the solution temperature was ±0.1 K. The solutions of the complexes in sulfuric acid were prepared immediately before the thermostatting. Sulfuric acid solutions were prepared from H_2SO_4 monohydrate ("kh.ch." (chemically pure) grade). The concentration of aqueous sulfuric acid was determined by acid-base titration with an error of up to 0.15%. The initial concentration of $(Cl)(H_2O)$IrTPP was 10^{-5} M.

The kinetics of complex oxidations was studied by "dissecting" the chemical reaction; the simple reactions that constitute the complex reaction were studied by the excess concentrations method. The effective rate constants and activation energies (k_{eff}, E_{eff}) were determined using the dependences $\log[(A_0 - A_\infty)/(A_\tau - A_\infty)] - f(\tau)$ and $\ln k_{eff}$–$f[1/T]$, respectively, while determining the mean square deviations by the least squares method with the Microsoft Excel program. Here, A_0, A_∞, A_τ are the optical densities of solutions at a working wavelength at τ equal to 0, at current τ, and at the time of complete reaction; T is the temperature. The reaction orders with respect to acid and the concentration-independent reaction rate constants were calculated using the dependence $\log k_{eff}^T - \log[H_2SO_4]$, where $[H_2SO_4]$ is the equilibrium concentration of sulfuric acid in concentrated aqueous H_2SO_4 [12]. The activation entropies ($\Delta S^{\#}$) of the reactions were determined by the Eyring equation for liquid systems for the second standard state.

RESULTS AND DISCUSSION

The chemical composition and stoichiometry of the complexes obtained by the reaction of porphyrin with chloroiridic acid was previously confirmed in [21]. The spectral data for the complexes in the UV–visible, IR, and NMR regions (see above) completely agree with the data of [21]. According to chromatographic data, the iridium(III) porphyrin complex readily undergoes the exchange of axial (not only molecular, but also covalently bound anionic) ligands. The axial ligand substitution reactions were observed when the complexes were dissolved in acids. In glacial acetic acid, $(Cl)(H_2O)$IrTPP exists in molecular form $(CH_3COO)(CH_3COOH)$IrTPP, which is slowly oxidized with atmospheric oxygen to the corresponding π-radical cation [21]. However, the substitution reaction can occur within a long period of time; then it becomes kinetically significant in other transformations of complexes. One of these transformations is the

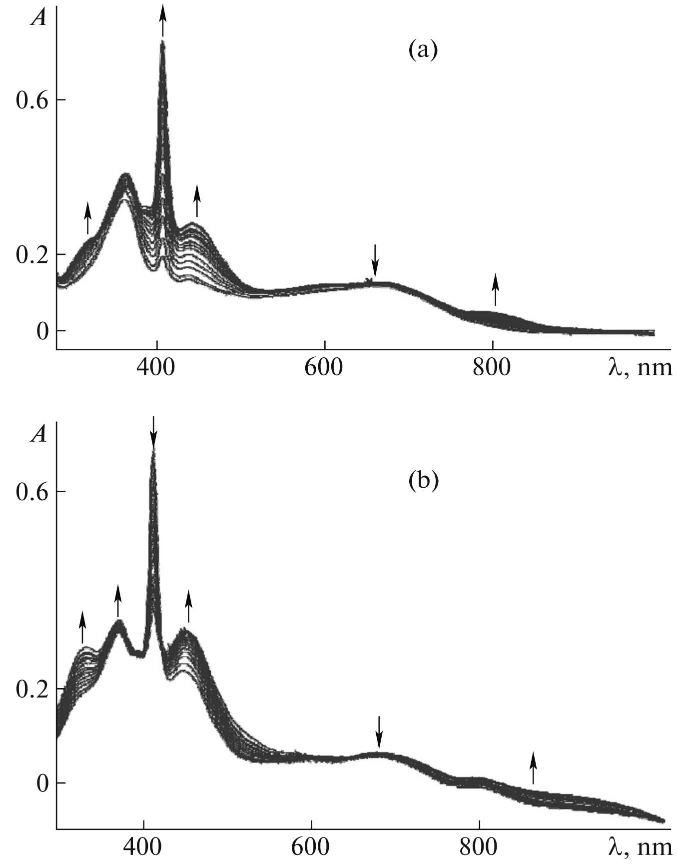

Fig. 1. UV–Vis spectrum of $(Cl)(H_2O)IrTPP$ in 16.85 M H_2SO_4 at 318 K and τ (s) (a) from 0 to 1000 and (b) from 1001 to 10000.

reaction of substitution of Cl^- and H_2O in $(Cl)(H_2O)IrTPP$ in the oxidation of the complex in CF_3COOH [21]. Therefore, here the similar chemical oxidation of Ir^{III} complexes in another oxidant (aerated H_2SO_4) was studied at all reagent concentrations and temperatures on an example of the $(Cl)(H_2O)IrTPP$ complex obtained in the highest yield.

In 16.79–18.09 M H_2SO_4, the UV–Vis of $(Cl)(H_2O)IrTPP$ differs from the spectra of the compound in AcOH and CF_3COOH. In 16.79 M H_2SO_4, the spectrum contains intense absorption with λ_{max} = 362 nm (the Soret (B-band) absorption) with a hypsochromic shifted by 80 nm compared with the spectrum in chloroform (initial line, Fig. 1). Also, there is a broadened Q-band with a maximum at ≈700 nm. The large hypsochromic shift of the Soret band, which is similar to that observed in the oxidation of the complex in CF_3COOH, points to the presence of the $[Ir^{IV}TPP]^{2+}$ cationic complex in solution. That is, the oxidation of the iridium(III) of $(Cl)(H_2O)IrTPP$, which occurs slowly in CF_3COOH, is completed at the moment of the dissolution of the complex in sulfuric acid:

$$(Cl)(H_2O)Ir^{III}TPP + O_2 + 2H_2SO_4 \xrightarrow{k_1} (HSO_4)_2Ir^{IV}TPP + HO_2^{\bullet} + Cl^- + H_3O^+. \qquad (1)$$

Then the reaction occurs slowly, and a change in the UV–Vis was recorded in two sequential series of spectral curves with clear-cut isosbestic points (Fig. 1). For the first series of spectra (Fig. 1a), a pronounced shoulder appeared at 323 nm and new band appeared and grew at 407 and 455 nm, while the 362-nm band remained unchanged. Growth of absorption with λ_{max} = 407 nm suggests the coordination of molecular oxygen [23, 24]. The coordination of O_2 by the $(Cl)RhTPP$ complex in concentrated H_2SO_4 and AcOH–H_2SO_4 mixtures was confirmed in [23] by the IR spectra and an experiment in solvents with lowered O_2 contents.

The second series of spectral bands (Fig. 1b) is characterized by a decrease in the intensity of the band of the complex coordinated with O_2 at 407 nm and growth of absorption at 323 nm and in the near IR region (≈915 nm). The new spectra correspond to the transition to the π-radical cation form of the iridium(IV) complex and point to the single-electron oxidation of its aromatic system. This is based on the highly specific and unambiguous interpretation of the UV–Vis of the metalloporhyrin π-radical cations [15, 17–21, 23]. In contrast to the EPR spectra of the latter, which do not always contain the signals of π-radical cations because of exchange interactions, the electronic spectra always suggest that they exist in solution.

The recording of two sequential series of spectra during the reaction of $(Cl)(H_2O)IrTPP$ with sulfuric acid allows the kinetic studies of each reaction separately. If the sum of the concentrations of the starting iridium complex and the product of its transformation is constant, the presence of isosbestic points in the spectrum series points to the transformation of two colored forms at every reaction stage. The linear concentration–time dependences in the coordinates of the first order equation $\log(C_0/C_\tau)$–τ demonstrate the preservation of the first order for MP at the first and second stages in all the ranges of H_2SO_4 concentration and temperature (298–318 K) under study. The k_{eff} values for the first reaction in the sequence, which are, on the average, 1×10^{-4}, 8×10^{-4}, and 4×10^{-3} s^{-1}, respectively, at 298, 308, and 318 K, are almost independent of the initial H_2SO_4 concentration, which is indicative of the zero order with respect to acid. The k_{eff} values for the second reaction (table) linearly correlate, in the logarithmic coordinates, with the equilibrium concentration of nonionized H_2SO_4 over the whole range of its concentrations for the reaction at 298 K (line *1*, Fig. 2) and in a narrower range for the reaction at 308 and 318 K (lines *2* and *3*, Fig. 2). In

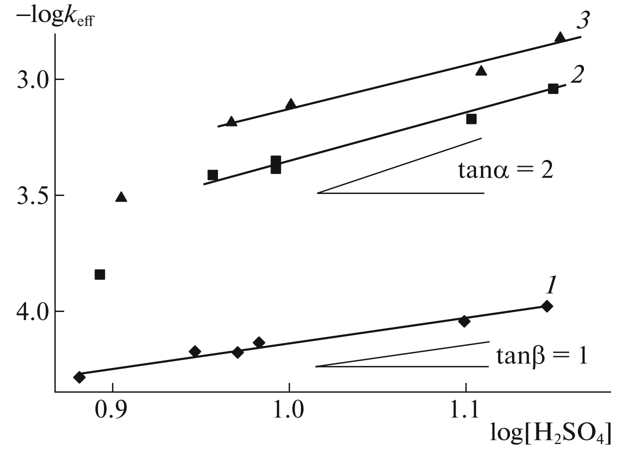

Fig. 2. Dependence $\log k^T_{eff}$–$\log[H_2SO_4]$ for the reaction of $(HSO_4)_2(O_2)IrTPP$ in 16.785–18.09 M H_2SO_4 at T, K: (*1*) 298, (*2*) 308, and (*3*) 318; ρ = 0.98–0.99.

addition, the reaction order (tan α) with respect to the equilibrium concentration of H_2SO_4, which is equal to one at 298 K, increases with temperature.

Thus, the equations of rate were found experimentally for two slow sequential stages of the reaction of $(Cl)(H_2O)IrTPP$ in H_2SO_4 at 298 K:

$$-dC_{(HSO_4)_2Ir^{IV}TPP}/dt = k_2C_{(HSO_4)_2Ir^{IV}TPP}, \quad (2)$$

$$-dC_{(HSO_4)_2(O_2)Ir^{IV}TPP}/d\tau = k_3C_{(HSO_4)_2(O_2)Ir^{IV}TPP}\,C_{H_2SO_4} \quad (3)$$

and at 308–318 K:

$$-dC_{(HSO_4)_2(O_2)Ir^{IV}TPP}/dt = k_3C_{(HSO_4)_2(O_2)Ir^{IV}TPP}\,C^2_{H_2SO_4}. \quad (4)$$

Equations (2) and (3) correspond to simple reactions of coordination of O_2 and single-electron oxidation of the complex with the coordinated O_2 molecule assisted by the acid proton:

$$(HSO_4)_2 \text{ equal to one } Ir^{IV}TPP + O_2 \xrightarrow{k2} (HSO_4)_2(O_2)Ir^{IV}TPP \text{ (slowly)}, \quad (5)$$

$$(HSO_4)_2(O_2)Ir^{IV}TPP + H_2SO_4 \xrightarrow{k_3} (HSO_4)_2Ir^{IV}TPP^{+\bullet} + HO_2^{\bullet} + HSO_4^- \text{ (slowly)}. \quad (6)$$

When the temperature of the sulfuric acid solution of the iridium complex increases, the equilibrium concentration of dissolved oxygen decreases. Under the conditions of oxygen deficiency, the single-electron oxidation of the Ir^{III} complex at the central atom (1) probably is not completed; therefore, the complex in the form of $(HSO_4)_2(O_2)Ir^{IV}TPP$ involved in slow oxidation of macrocycle (6) is in equilibrium with its form that is not oxidized at the central atom $(HSO_4)(O_2)Ir^{III}TPP$. If, in the equation of rate for suggested stage (6) similar to the experimental equation (3), the concentration of $(HSO_4)_2(O_2)Ir^{IV}TPP$ is expressed in terms of the constant of the above-men-

Effective kinetic parameters of the oxidation of $(HSO_4)_2(O_2)Ir^{IV}TPP$ in H_2SO_4

$C^0_{H_2SO_4}$, % (M)	$[H_2SO_4]$, M	T, K	$k_{eff} \times 10^4$, s^{-1}	E_{eff}, kJ/mol	$-\Delta S^{\#}_{eff}$, J/(mol K)
90.57 (16.785)	7.61	298	0.54 ± 0.05	70	100
	7.83	308	1.5 ± 0.05		
	8.045	318	3.2 ± 0.3		
91.72 (17.05)	8.84	298	0.72 ± 0.07	87	39
	9.07	308	3.9 ± 0.2		
	9.29	318	6.7 ± 0.5		
92.39 (17.20)	9.61	298	0.76 ± 0.04	92	22
	9.83	308	4.5 ± 0.4		
	10.03	318	8.0 ± 0.7		
95.03 (17.77)	12.55	298	0.90 ± 0.08	97	2
	12.69	308	6.6 ± 0.6		
	12.82	318	11.0 ± 0.1		
96.00 (18.09)	14.00	298	1.1 ± 0.1	102	15
	14.12	308	9.0 ± 1.0		
	14.25	318	15.0 ± 1		

For E_{eff} and $-\Delta S^{\neq}_{eff}$, the tentative values were determined for the temperature range 308–318 K.

tioned equilibrium, we arrive at an equation with a higher (second) order with respect to sulfuric acid.

According to the suggested theoretical scheme of simple reactions in the complex transformation of $(Cl)(H_2O)Ir^{III}TPP$ in concentrated H_2SO_4, which acts both as a solvent and as a single-electron oxidant, at first the central metal cation is quickly and irreversibly (at 298 K) oxidized to Ir^{IV}. Simultaneously, the axial ligands are replaced by HSO_4^- ions due to their large ($\sim 10^4$) excess in solution relative to the complex. The easy fast exchange of axial ligands in the iridium(III) porphyrin complexes in different solvents was confirmed by many authors. We can cite studies of the dependence of the axial environment in complexes on pH of the medium; the interaction of Ir(CO)(Cl)OEP with pyridine, *N*-(*n*-butyl)imidazole, and 1-imidazoleacetic acid [25]; and the transformations of the water-soluble aqua and hydroxo derivatives of Ir^{III} tetra(sulfophenyl)porphyrins in aqueous and methanol solutions [26, 27].

Then the quadruply charged iridium complex coordinates O_2 without participation of H_2SO_4, transforming into a complex with an extended coordination sphere $(HSO_4)_2(O_2)Ir^{IV}TPP$. The complex is oxidized at the macrocyclic ligand under the action of activated molecular oxygen in the first coordination sphere with the assistance of sulfuric acid protons, forming the π-radical cation.

The rate constant of the oxidation of the aromatic system in $(HSO_4)_2(O_2)Ir^{IV}TPP$ into the π-radical cation k_3^{298}, which does not depend on the H_2SO_4 concentration, is 7.2×10^{-6} mol^{-1} L s^{-1}.

The electron removal location during the chemical oxidation of $(Cl)(H_2O)IrTPP$ with atmospheric oxygen in proton-donor solvents depends on the medium acidity and the nature of the axial ligands. In 100% AcOH ($pK_a = 4.76$ [28]), the complex slowly forms the π-radical cation; in CF_3COOH ($pK_a = 0.23$ [29]), the oxidation at the central metal cation to Ir^{IV} takes place; and in concentrated H_2SO_4 ($pK_{a1} = -3$ [30]), both processes occur in sequence. The axial composition of the Ir^{III} complex varies in these media. The coordinated molecules and trifluoroacetic anions, which are electron acceptors, produce the *cis*-effect on the coordinated macrocycle and decrease the π-electron density on its atoms; therefore, the oxidation of the Ir^{III} complex does not occur at the macrocycle. The mixed electron donor-acceptor nature of hydrosulfate ions in $(HSO_4)_2Ir^{IV}TPP$, which have both lone electron pairs and energy-accessible vacant *d* orbitals, combined with high acidity of sulfuric acid, favors the occurrence of two sequential oxidations (1) and (6) (at the central atom and macrocycle). The ease of the transition $Ir^{III} \rightarrow Ir^{IV}$ was confirmed by the electrochemical study [31], according to which the redox couple $[(TPP)Ir]^+/[(TPP)Ir]^{2+}$ has a relatively low energy $E_{1/2} \sim 1.4$ V.

The $(Cl)(H_2O)IrTPP$ complex is less stable than its rhodium analog (Cl)RhTPP in the chemical oxidations in aerated acids. Because of lower reactivity in the axial directions and the ensuing electron-excessive state of the macrocycle, in a mixed solvent AcOH–3–5 M H_2SO_4, (Cl)RhTPP forms an H^+-associated form with coordinated O_2 $(Cl)(O_2)RhTPP\cdots H^+\cdots R$ instead of exchanging the axial ligands and is oxidized to the $(HSO_4)RhTPP^{+\bullet}$ π-radical cation without any change in the oxidation state of Rh only in solvents with high proton concentration (concentrated H_2SO_4) [23]. A definite role is also played by the more effective participation of the Rh atom in the π-interaction with the macrocycle because of its higher electronegativity compared with that of Ir^{III}. The latter is reflected in the hypsochromic position (535 nm) of the $\pi \rightarrow \pi^*$ transition band Q(0,1) in the spectrum of (Cl)RhTPP in organic solvents compared with that of the Ir complex (549 nm). The sequential electrochemical oxidation of (Cl)RhTPP with triphenylphosphine at 0.98 and 1.36 V gives the π-radical cation and the π-radical dication, respectively [32, 33]. The Rh^{IV} compound was obtained only with *N*-converted porphyrin by treatment of $(NCTPP)Rh(CO)_2Rh(CO)_2Cl$ with metallic I_2 [34].

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