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Properties of Chemically Generated π-Radical Cations and Molecules of (*meso*-Phenyl-β-Octaethylporphyrinato)rhenium(V) with Axial Molecular Oxygen

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Abstract—The state of existence and reactions of stable rhenium(V) complexes with β-octaethylporphin (O=Re(OPh)OEP, O=Re(Cl)OEP) and its *meso*-diphenyl-substituted derivatives (O=Re(Cl)^{5,15}DPOEP) in concentrated H_2SO_4 at 318–348 K were studied. It was found that O=Re(Cl)^{5,15}DPOEP undergoes slow single-electron oxidation at the aromatic ligand to give π-radical cation. The oxidation is accompanied by replacement of the axial Cl^- ligand by the hydrogen sulfate ion present in excess. Full kinetic description of the intricate oxidation reaction of the complex involving atmospheric oxygen was obtained and parameters of simple reactions that constitute the intricate process were determined. In the case of O=Re(Cl)OEP and O=Re(OPh)OEP, the reaction stops after the formation of the cationic complex with axially coordinated oxygen and outer-sphere chloride ion O=Re(O_2)OEP$^+$ Cl^-. The effect of the nature of axial and macrocyclic ligands in rhenium(V) porphyrins on the processes in sulfuric acid solutions of these compounds was established.

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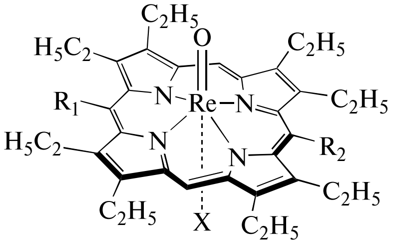
The metal complex catalysis is based on coordination and activation of the coordinated molecules. In the case of catalysis by metal porphyrins (MP), owing to the presence of easily polarizable macrocyclic aromatic system, especially important are their intermediate oxidized or reduced forms. Catalytic processes are frequently encountered in the porphyrin chemistry [1–9]. Therefore, the task of identification of the redox forms of MP becomes more and more topical.

It was established [10–14] that single-electron oxidized π-radical cations can be chemically generated from MP on treatment with aerated sulfuric acid. As in the electrochemical oxidation, the crucial factors determining the feasibility of these transformations are the nature of the metal cation and the electronic state of the macrocycle, which can be changed by functional substitution at its periphery. The oxidation with air oxygen of the complexes H_2TPP (TPP is the 5,10,15,20-tetraphenyl-21H,23H-porphin dianion) with Ru^{IV} and Os^{II} in AcOH–H_2SO_4 mixtures [10] and with Rh^{III} in concentrated aqueous H_2SO_4 [11] at temperatures of >340 K was studied. The formation of the oxidized form of the complexes (Cl)Re^{III}TPP in AcOH–3 M H_2SO_4 and [O=Re^VTPP]$_2$O in hot AcOH–5–10 M H_2SO_4 mixtures was detected [12]. In all of the mentioned cases, the aromatic macrocycle is the reaction center of oxidation, and only in OsTPP, the oxidation involves the central metal atom. The relationship between the stability against oxidation, the reaction route, and the chemical structure of the macrocyclic complex had been considered only in relation of Pd^{II} porphyrin complexes [13, 14]. The recent advances in the synthesis of rhenium porphyrin complexes [15–20], which are distinguished by diversity of coordination polyhedra and substituent system in the macroheterocyclic ligand, provide the possibility to continue research along this line with Re complexes.



1, R_1, R_2 = H, X = OPh, O=Re(OPh)OEP
2, R_1, R_2 = H, X = Cl, O=Re(Cl)OEP
3, R_1, R_2 =Ph, X = Cl, O=Re(Cl)^{5,15}DPOEP

The present communication describes the results of studies of the chemical structure and spectral properties of the products of oxidation of the rhenium(V) complexes with 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphin H_2OEP (**1**, **2**) and its 5,15-diphenyl derivative $H_2^{5,15}$DPOEP (**3**) with atmospheric oxygen in concentrated sulfuric acid.

EXPERIMENTAL

(2,3,7,8,12,13,17,18-Octaethylporphinato)(oxo)(phenoxo)rhenium(V) O=Re(OPh)OEP (1). H_2OEP and H_2ReCl_6 in 1 : 5 molar ratio were refluxed in phenol at 454 K for 9 h. Completion of the complex formation reaction was detected by spectrophotometry. The reaction mixture was transferred into CH_2Cl_2, the resulting solution was washed many times by warm water to remove phenol, concentrated, and chromatographed on an Al_2O_3 column (Brockmann activity II) using CH_2Cl_2 as the eluent. This gave two zones, a pink zone containing H_2OEP and a green-brown zone. The substance of the second zone was once again chromatographed on a silica gel column (40/100 Chemapol). Elution with benzene produced two zones, a pale orange impurity zone and a green-brown zone of the target complex strongly retained at the start. The complex zone was eluted with a CH_2Cl_2–C_2H_5OH mixture (1 : 1 v/v), and the resulting solution was again chromatographed on a silica gel column (40/100 Chemapol) using dichloromethane as the eluent. This gave O=Re(OPh)OEP in 70% yield.

UV-Vis (CH_2Cl_2), λ_{max}, nm: 613 sh, 580, 469, 343; (AcOH): 634 sh, 597, 490, 341.

IR (KBr), ν, cm^{-1}: pyrrole rings, 1468 (ν(C=N)), 1376 (ν(C–N)), 1057 (C_3–C_4, ν(C–N)); alkyl groups, 1317 (δ(C–H)), methine groups, 1273, 1223 (δ(C–H)), 873, 844, (γ(C–H)); coordination center, 959 (Re=O), 454, 466 (Re–N), 670 (Re–O); axial ligand, 1589, 1451 (–Ph).

^1H NMR (C_6D_6), δ, ppm: 1.83 (m, CH_3), 4.03 (m, 16 H, CH_2), 4.43 (m, 32 H, CH_2), 9.51 (m, 8H, *meso*), 10.77 (m, 4H, *meso*), 7.04 (s, $2H_o$ (OPh)), 6.95 (s, $2H_m$ (OPh)), 6.85 (s, $1H_p$ (OPh)).

^1H–^1H 2D COSY NMR (C_6D_6), δ, ppm: 4.43 (m, 32H, CH_2)–1.83 (m, CH_3), 4.03 (m, 16H, CH_2)–1.83 (m, CH_3).

For $C_{42}H_{49}N_4O_2Re$ anal. calcd. (%): C, 60.94, H, 5.93, N, 6.77.

Found (%): C, 62.17; H, 6.31; N, 7.15.

(2,3,7,8,12,13,17,18-Octaethylporphinato)(oxo)(chloro)rhenium(V) O=Re(Cl)OEP (2). The complex was prepared from O=Re(OPh)OEP by passing HCl gas for 10 min through a solution of O=Re(OPh)OEP in CH_2Cl_2. During this period, the solution color changed from green-yellow to pink. The yield was 100%.

UV-Vis (CH_2Cl_2), λ_{max}, nm (logε): 620 (3.90), 518 (4.30), 347 (4.92).

IR (KBr), ν, cm^{-1}: pyrrole rings, 1468 (ν(C=N)), 1376 (ν(C–N)), 1057 (C_3–C_4, ν(C–N)); alkyl groups, 1316 (δ(C–H)); methine groups, 1223, 1271 (δ(C–H)), 846, 854, 871 (γ(C–H)); coordination center, 965 (Re=O), 467 (Re–N).

^1H NMR ($CDCl_3$), δ, ppm: 2.13 (m, 24H, CH_3), 4.36 (m, 16H, CH_2), 10.94 (m, 2H, *meso*).

^1H–^1H 2D COSY NMR ($CDCl_3$), δ, ppm: 4.36 (m, 16H, CH_2)–2.13 (m, 24H, CH_3).

(5,15-Diphenyl-2,3,7,8,12,13,17,18-octaethylporphinato)(oxo)(chloro)rhenium(V), O=Re(Cl)^{5,15}DPOEP (3). The synthesis and isolation procedures were similar to the procedure presented above for compound **1** with $H_2^{5,15}$DPOEP being used instead of H_2OEP. The synthesis time was 6 h. Chloroform served as the eluent for chromatography. The yield was 75%.

UV-Vis (CH_2Cl_2), λ_{max}, nm (logε): 625 (3.70), 525 (4.15), 354 (4.75).

IR (KBr), ν, cm^{-1}: phenyl groups, 3059, 3022 (ν(C–H)); 1600, 1532, 1491 (ν(C=C)); 1125, 1073 (δ C–H); 702, 742 (γ(C–H)); pyrrole groups, 1465 (ν(C=N)), 1384 (ν(C–N)), 1062 (C_3–C_4, ν(C–N); alkyl groups, 1400, 1341 (δ(C–H)); methine groups, 1274 (δ(C–H)); 838, 861 (γ(C–H)); coordination center, 962 (Re=O), 467 (Re–N).

^1H NMR ($CDCl_3$), δ, ppm, *J*, Hz: 1.56 (br. s, 14H, CH_3), 1.95 (t, 10H, CH_3), 2.70 (br.s, 6H, CH_2), 4.20 (m, 10 H, CH_2), 7.55 (q, $1H_p$, $J = 7.3$); 7.73 (q, $1H_p$, $J = 7.3$), 7.85 (*m*, $2H_m$), 7.91 (m, $2H_m$), 8.20 (d, $2H_o$, $J = 8.1$), 8.29 (d, $2H_o$, $J = 8.1$), 10.82 (m, 2H, *meso*).

^1H–^1H 2D COSY NMR ($CDCl_3$), δ, ppm, *J*, Hz: 2.70 (br.s, 6H, CH_2)–1.95 (t, 10H, CH_3); 4.20 (m, 10H, CH_2)–1.56 (br.s, 14H, CH_3); 4.20 (m, 10H, CH_2)–1.95 (t, 10 H, CH_3); 7.85 (m, $2H_m$)–7.55 (q, $1H_p$, $J = 7.3$); 7.91 (m, $2H_m$)–7.73 (q, $1H_p$, $J = 7.3$); 8.20 (d, $2H_o$, $J = 8.0$)–7.85 (m, $2H_m$); 8.29 (d, $2H_o$, $J = 8.1$)–7.91 (*m*, $2H_m$).

For $C_{48}H_{52}N_4OClRe$ anal. calcd. (%): C, 62.51; H, 5.64; N, 6.08.

Found (%): C, 61.05, H, 5.45, N, 5.41.

The solid samples of the products were isolated from solutions after chromatography by evaporation of the solvent at room temperature. The individual nature and the purity of the compounds were confirmed by TLC on Silufol silica gel using a 10 : 1 CH_2Cl_2–C_2H_5OH mixture for compounds **1** ($R_f = 0.52$), **2** ($R_f = 0.64$), and **3** ($R_f = 0.50$).

The UV-Vis spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer, the IR spectra were measured on a Vertex 80v spectrophotometer; and ^1H NMR spectra were run on a Bruker Avance III-500 spectrometer. Elemental analysis was performed on CHNS-O Analyzer Flash EA 1112 Series. The UV-Vis spectra were recorded as plots and tables for the subsequent mathematical processing.

The decrease in the substance concentrations in kinetic experiments was monitored by spectrophotometry. The measurements were carried out in 1-cm thick cells placed into a special chamber maintained in a thermostat in the cell holder of the spectrophometer.

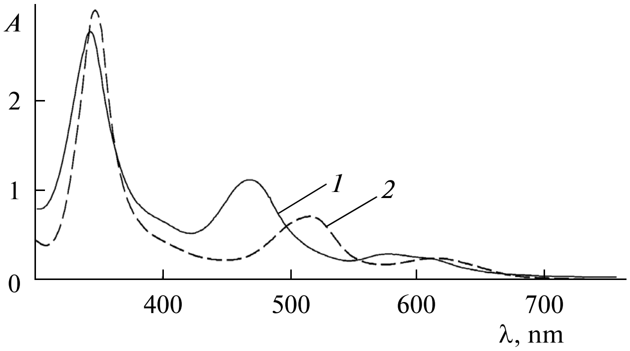


Fig. 1. UV-Vis spectra of compounds (*1*) **1** and (*2*) **2** in CH_2Cl_2.

The error of determination of the solution temperature was ±0.1 K. Solutions of the complexes in sulfuric acid were prepared immediately before being placed into the thermostat. The oxidation kinetics of the complexes was studied by the method of excess concentrations.

The rate constants and activation energies (k_{eff}, k, E) were determined together with the root-mean-square deviations by the least squares method using Microsoft Excel software and the dependences $\log[(A_0 - A_\infty)/(A_\tau - A_\infty)] - f(\tau)$, $\log k_{\mathrm{eff}} - f[H_2SO_4]$, $\ln k - f[1/T]$ where A_0, A_∞, and A_τ are the solution absorbances at the operating wavelength at zero time, current time τ, and the time of completion of the reaction, respectively; $[H_2SO_4]$ is the equilibrium concentration of non-ionized H_2SO_4 molecules in concentrated aqueous sulfuric acid [21]; T is temperature.

The activation entropy ($\Delta S^{\neq}_{\mathrm{eff}}$) of the reaction was determined by the Eyring equation as applied to liquid systems for the second standard state.

Sulfuric acid of high concentration was prepared from reagent grade H_2SO_4. The concentration of aqueous sulfuric acid was determined by acid–base titration with an error of not more than 0.15%. Acetic acid with a 100% concentration was prepared by fractional unfreezing of glacial AcOH (water content of 0.015%).

RESULTS AND DISCUSSION

According to physicochemical analysis data (Experimental), the synthesized complexes were identified as seven-coordinate O=Re(OPh)OEP (**1**), O=Re(Cl)OEP (**2**), and O=Re(Cl)^{5,15}DPOEP (**3**). The UV-Vis spectra of the compounds refer to the so-called hyper type [22] and characterize the metal porphynins as complexes of rhenium in the oxidation state of +5. Namely, apart from the long-wavelength Q and B (Soret) bands for $\pi \rightarrow \pi^*$ transitions between the frontier molecular orbitals typical of $M^{II}P$ and $Re^{III}P$, the spectra have an additional intense absorption band with a maximum at about 350 nm (Fig. 1), which is interpreted in the hyper type spectra as a charge transfer band [23].

^1H NMR spectra of compounds **1**–**3** (Experimental) correspond to 1 : 1 complexes. It was found experimentally that compound **1** exists in neutral solutions in equilibrium with an μ-oxodimer impurity. The ^1H NMR spectrum in C_6D_6 (Fig. 2) exhibits two signals for H_{meso} protons at 10.77 and 9.51 ppm, the latter (located at higher field) was assigned to μ-oxo dimer by analogy with $[O{=}Re^{V}TPP]_2O$ [20]. The lack of correlation between them in the ^1H–^1H 2D COSY (Experimental) and ^1H–^1H 2D ROESY (Fig. 2) spectra in C_6D_6 implies that they belong to different compounds. Compounds **2** and **3** with axial chloride ion do not form species of this type in solutions, which, together with high stability of the coordination center, allows one to study their forms chemically generated in concentrated sulfuric acid. In acids, compound **1** also exists exclusively as a monomer.

Upon dissolution in 16.8–18.2 M H_2SO_4, compounds **1**, **2**, and **3** form, as will be seen below, products of different chemical structure. The UV-Vis spectrum of compound **3** in acid (brown-colored solution) differs from the spectrum in CH_2Cl_2: the Soret and charge transfer bands are shifted to 361 and 460 nm, and a new intense absorption occurs at ~860 nm. Noticeable transformation of the spectrum of **3** in sulfuric acid takes place at temperatures of >318 K. The spectra change by forming strictly three series of bands, each having specific isosbestic points (Fig. 3), which attests to occurrence of three consecutive reactions. For each reaction, transition between two colored compounds can be stated. The isolation of three separate series of bands in the overall spectral pattern made it possible to record the UV-Vis spectra of the intermediate and final products (Table 1) and apply the dissection method to the complex chemical reaction to study its kinetics.

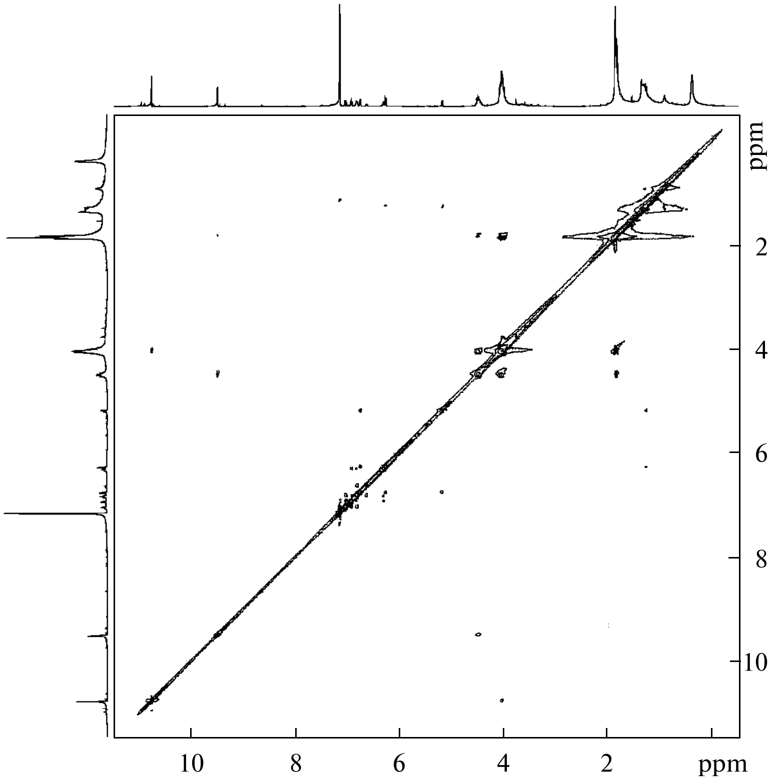


Fig. 2. ^1H–^1H 2D ROESY NMR spectrum of compound **1** in C_6D_6.

The presence of long-wavelength absorption and great hypsochromic shift of the Soret band in the initial spectrum of compound **3** in H_2SO_4 (Fig. 3a) with respect to the spectra in CH_2Cl_2 and AcOH may indicate the presence of coordinated molecular oxygen [24–26] and extended first coordination sphere of the dissolved complex—O=Re(Cl)$(O_2)^{5,15}$DPOEP, the concentration of which decreases in the first consecutive reaction during maintenance in the thermostat.

In the second series of the spectra (Fig. 3b), the final line is similar to the spectrum of the initial molecular form of **3** in CH_2Cl_2 with a maximum of the charge transfer band at about 560 nm. The solution color changes from brown to pink. The pronounced

Table 1. UV-Vis spectra of individual species formed from O=Re(Cl)^{5,15}DPOEP and O=Re(X)OEP (X = Cl or OPh) in concentrated sulfuric acid

Complex species in the solution	λ_{max}, nm				Intensity ratio
	I	II	III	IV	
O=Re(Cl)^{5,15}DPOEP^a	–	625	525	354	**IV > III > II**
O=Re(Cl)$(O_2)^{5,15}$DPOEP	865	–	–	361	**IV > I**
O=Re$(O_2)^{5,15}$DPOEP$^+$Cl$^-$	–	–	460	332	**IV > III**
O=Re$(HSO_4)^{5,15}$DPOEP	–	774	560	322	**IV > III > II**
O=Re$(HSO_4)^{5,15}$DPOEP$^{\bullet+}$	–	772	520	316	**IV > III > II**
O=Re(X)^{5,15}DPOEP$^{\bullet+b}$	–	–	467	368	**IV > III**
O=Re(O_2)OEP$^+$Cl$^-$	789	–	455	325	**IV > III > I**
O=Re(O_2)OEP$^+$OPh$^-$	790	–	456	325	**IV > III > I**

^{a} In CH_2Cl_2; ^{b} in C_2H_5OH after isolation from H_2SO_4 after completion of the reaction.

dependence of the positions of the UV-Vis bands of $\mathrm{Re^V}$ complexes, which is obvious upon consideration of complexes **1** and **2** (Experimental), suggests that the second consecutive reaction involves replacement of the axial ligand by $\mathrm{HSO_4^-}$ present in the solution in a large excess with respect to the porphyrin complex.

As the reaction mixture is further kept in the thermostat (Fig. 3c), the solution color changes again to brown and the general background of the spectrum at 380–550 nm grows. These changes in the UV-Vis spectrum attest to the formation of the rhenium complex species oxidized at the macrocycle similarly to chemically generated radical species formed from other metal complexes [10–14].

According to Figs. 4 and 5, the strictly first order with respect to the concentration of the complex was established for each of the consecutive reactions, while the order with respect to the equilibrium concentration of sulfuric acid [21] was 0, 1, and 1 for the first, second, and third consecutive reactions, respectively:

$$-dC_{\mathrm{O=Re(Cl)(O_2)^{5,15}DPOEP}}\big/d\tau = k_1C_{\mathrm{O=Re(Cl)(O_2)^{5,15}DPOEP}}, \qquad (1)$$

$$-dC_{\mathrm{MP}}/d\tau = k_2C_{\mathrm{MP}}C_{\mathrm{H_2SO_4}}, \qquad (2)$$

$$\begin{aligned}&-dC_{\mathrm{O=Re(HSO_4)^{5,15}DPOEP}}\big/d\tau\\ &= k_3C_{\mathrm{O=Re(HSO_4)^{5,15}DPOEP}}C_{\mathrm{H_2SO_4}}.\end{aligned} \qquad (3)$$

Relying on the rate equations thus obtained, it is possible to write down the sequence of three slow reactions (5)–(7), which are preceded by the fast irreversible step of attachment of an oxygen molecule to the axial axis of the molecule (4):

$$\begin{aligned}&\mathrm{O{=}Re(Cl)^{5,15}DPOEP + O_2}\\ &\rightarrow \mathrm{O{=}Re(Cl)(O_2)^{5,15}DPOEP}, \text{ fast},\end{aligned} \qquad (4)$$

$$\begin{aligned}&\mathrm{O{=}Re(Cl)(O_2)^{5,15}DPOEP}\\ &\xrightarrow{k_1} \mathrm{O{=}Re(O_2)^{5,15}DPOEP^+ \cdot Cl^-}, \text{ slow},\end{aligned} \qquad (5)$$

$$\begin{aligned}&\mathrm{O{=}Re(O_2)^{5,15}DPOEP^+ \cdot Cl^- + H_2SO_4}\\ &\xrightarrow{k_2} \mathrm{O{=}Re(HSO_4)^{5,15}DPOEP + O_2 + HCl}, \qquad (6)\\ &\text{slow},\end{aligned}$$

$$\begin{aligned}&\mathrm{O{=}Re(HSO_4)^{5,15}DPOEP + O_2 + H_2SO_4}\\ &\xrightarrow{k_3} \mathrm{O{=}Re(HSO_4)^{5,15}DPOEP^{\cdot+}}\\ &+ \mathrm{HO_2^{\cdot} + HSO_4^-}, \qquad (7)\\ &\text{slow}.\end{aligned}$$

According to this scheme, in $\mathrm{H_2SO_4}$, the rhenium complex having peroxo-coordinated molecular oxygen in the axial position is slowly converted to the outer-sphere chloride complex **(4)** with a zero reaction order with respect to $\mathrm{H_2SO_4}$.

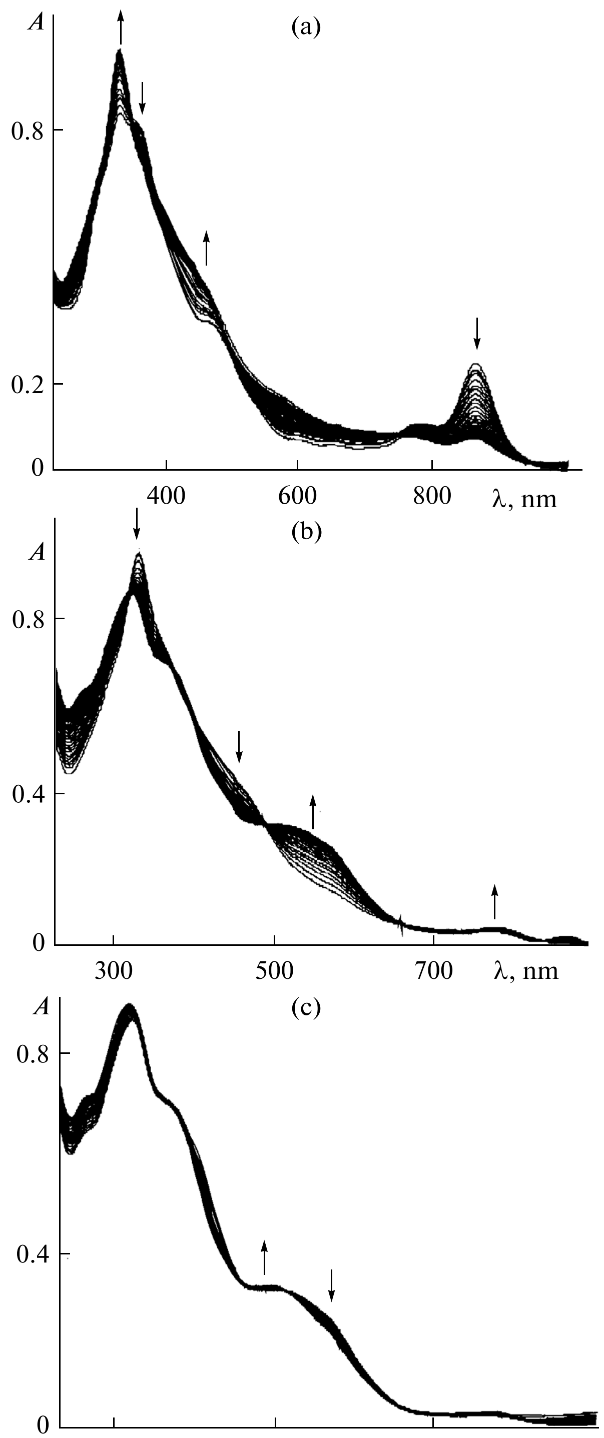


Fig. 3. Change of the UV-Vis spectrum of compound *3* in 18.14 M $\mathrm{H_2SO_4}$ at 338 K at time τ (s) varying (a) from 0 to 682, (b) from 683 to 3482, (c) from 3482 to 6602.

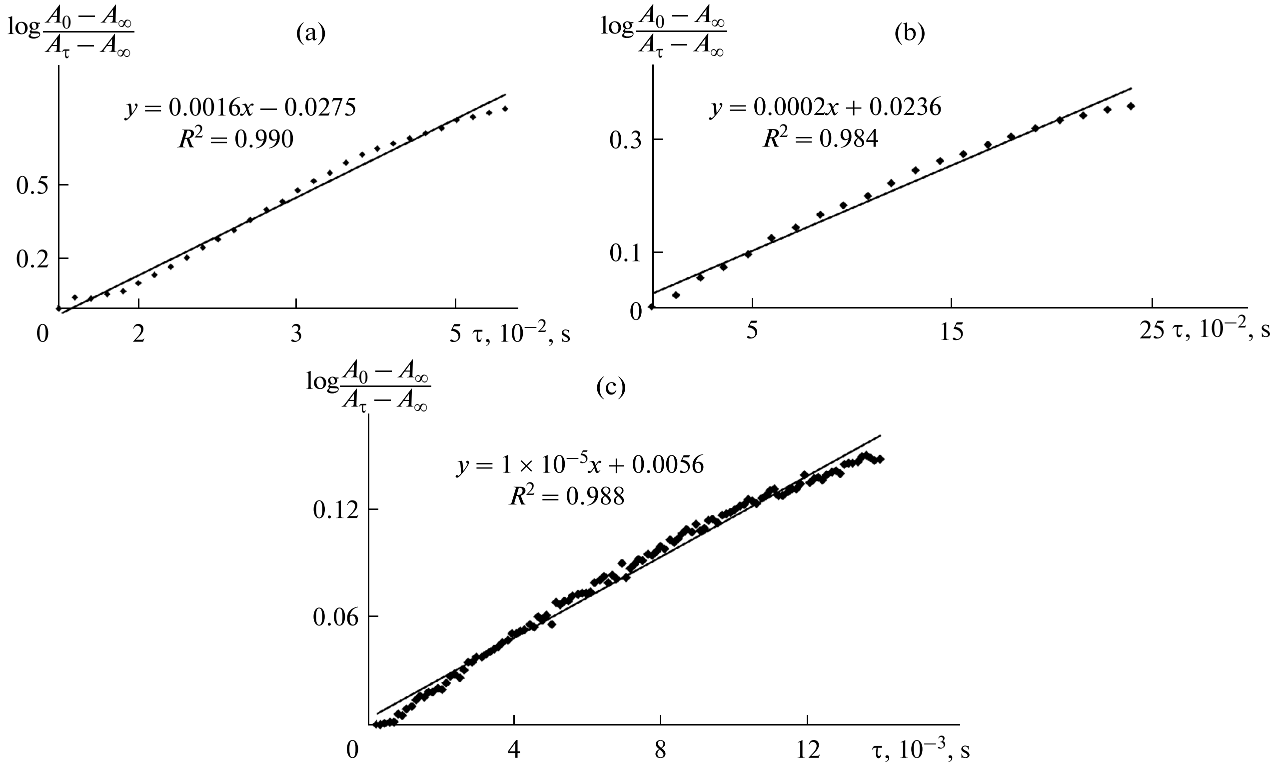


Fig. 4. Dependence $\log\frac{A_0 - A_\infty}{A_\tau - A_\infty}$–τ for the three consecutive reactions of compound **3** in 18.2 M H_2SO_4 at 328 K (a, b, and c, respectively). τ_∞ for the first and second reactions are equal to τ_0 of the second and third reactions, respectively.

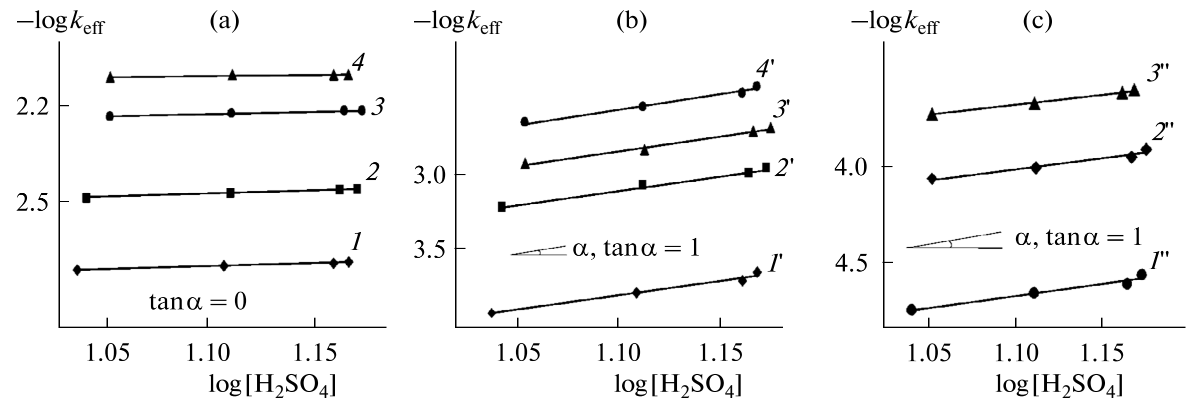
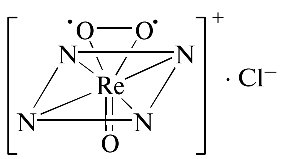


Fig. 5. Dependences $\log k_{\text{eff}}$–$\log[H_2SO_4]$ for the (a) first, (b) second, and (c) third consecutive reactions in the system O=Re(Cl)^{5,15}DPOEP–H_2SO_4. *T*, K: (1, 1', 1'') 318; (2, 2', 2'') 328; (3, 3', 3'') 338; (4, 4', 4'') 348 (ρ = 0.97–0.99).



4

This species coordinates the HSO_4^-, ion present in excess to the vacant coordination site in the first coordination sphere, resulting in displacement of the O_2 molecule and the subsequent single-electron oxidation with air oxygen with assistance of acid protons. Due to the *trans*-effect, the molecular complex of O_2 with O=Re(HSO_4)^{5,15}DPOEP is less stable than O=Re(Cl)(O_2)^{5,15}DPOEP with less strongly bonded *trans*-ligand Cl^-.

The stability of all of the intermediate rhenium complex species at the Re–N bonds is confirmed by the fact that the $H_4^{5,15}DPOEP^{2+}$ cations having rather specific UV-Vis spectrum were not detected in any of

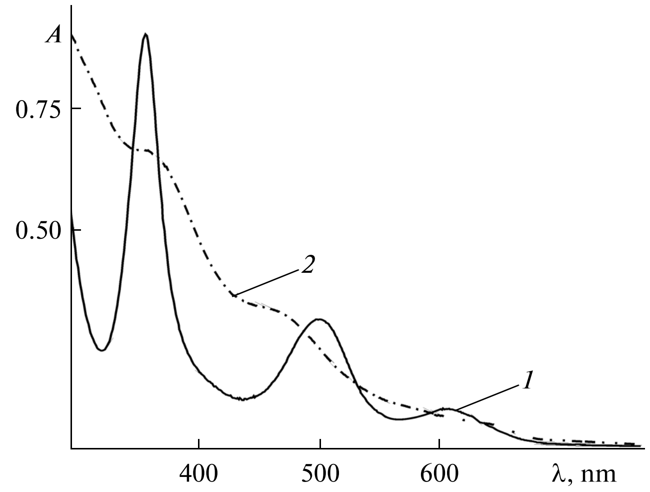


Fig. 6. UV-Vis spectrum of compound **3** isolated from H_2SO_4: in (*1*) CH_2Cl_2 and (*2*) C_2H_5OH.

the process steps. To confirm the composition of the final product of the complex reaction, the product was recrystallized from the reaction mixture by pouring the mixture onto ice, washed to remove the acid, and dissolved in C_2H_5OH. The UV-Vis spectrum of the solution (Table 1, Fig. 6) exhibits the absorption bands at ≈500 and 350 nm and increased spectral background at 350–450 nm, indicating the presence of axially coordinated hydrogen sulfate ion and the π-radical cation form of the complex, respectively.

The summation of equations (4)–(7) gives the overall oxidation equation of compound **3** with aerated H_2SO_4:

$$\begin{gathered}\mathrm{O{=}Re(Cl)^{5,15}DPOEP} + \mathrm{O_2} + \mathrm{H_2SO_4} \\ \rightarrow \mathrm{O{=}Re(HSO_4)^{5,15}DPOEP^{\bullet +}} + \mathrm{HO_2^{\bullet}} + \mathrm{Cl^-}.\end{gathered} \tag{8}$$

The rate constants k_1, k_2, k_3 and the activation parameters for each reaction in the system O=Re(Cl)^{5,15}DPOEP–H_2SO_4 are summarized in Table 2. The release of charged H^+ and Cl^- during the activation in the second slow reaction step is consistent with the large negative value of $\Delta S^{\#}$, while the high stability of metal porphyrin against oxidation is consistent with high energy expenditure for the activation in the third (last) slow step with very low rate constant.

Upon dissolution of compounds **1** and **2** in 16.8–18.2 M H_2SO_4, the UV-Vis spectra of the solutions exhibit absorption bands with λ_{max} of 325, 456, 790 and 325, 455, 789 nm, i.e., the spectral pattern is similar to that of the UV-Vis spectrum of **3** recorded under the same conditions. However, within 3 min (compound **1**) and 1 min (compound **2**) at 298 K, the spectrum changes (Fig. 7): the absorption at 800 nm disappears, while the other two bands become more intense. On further maintenance in the thermostat and temperature rise to 363 K, the UV-Vis spectrum remains unchanged (Table 1).

The observed transformations are similar to the changes in the spectra during the first step of reaction of compound **3** in concentrated sulfuric acid (Fig. 3a) and, hence, they correspond to the formation of O=Re(O_2)OEP$^+$ · OPh$^-$ and O=Re(O_2)OEP$^+$ · Cl$^-$. The rate constants (k_{eff}) at 17.77 mol/L at 298 K were found to be 1.6×10^{-2} and 4.2×10^{-2} s^{-1} for **1** and **2** (Fig. 7), respectively. They are higher than k_{eff} for the formation reactions of O=Re(O_2)MPOEP$^+$ · Cl$^-$ (5.8×10^{-4} s^{-1}) [27] and O=Re(O_2)^{5,15}DPOEP$^+$ · Cl$^-$ (equation (5)) (5.6×10^{-3} s^{-1}). The spectra of the transformation products of **1** and **2** in dichloromethane after reprecipitation from their sulfuric acid solutions onto ice (λ_{max} of 498 and 350 nm) do not coincide with the

Table 2. Kinetic parameters of the consecutive reactions of O=Re(Cl)^{5,15}DPOEP in H_2SO_4

T, K	$k_1 \times 10^3$, s^{-1}	$k_2 \times 10^5$, mol^{-1} L s^{-1}	$k_2 \times 10^5$, mol^{-1} L s^{-1}
318	1.24	0.85	–
328	1.92	2.13	0.087
338	4.16	2.87	0.5
348	5.91	3.81	1.3
298[a]	0.18	0.096	0.0002
E, kJ/mol	54 ± 11	54 ± 15	127 ± 23
$-\Delta S^{\#}$, J/(mol K)	140 ± 30	180 ± 35	50 ± 6

[a] Found by extrapolation of the dependence log$k$–1/T.

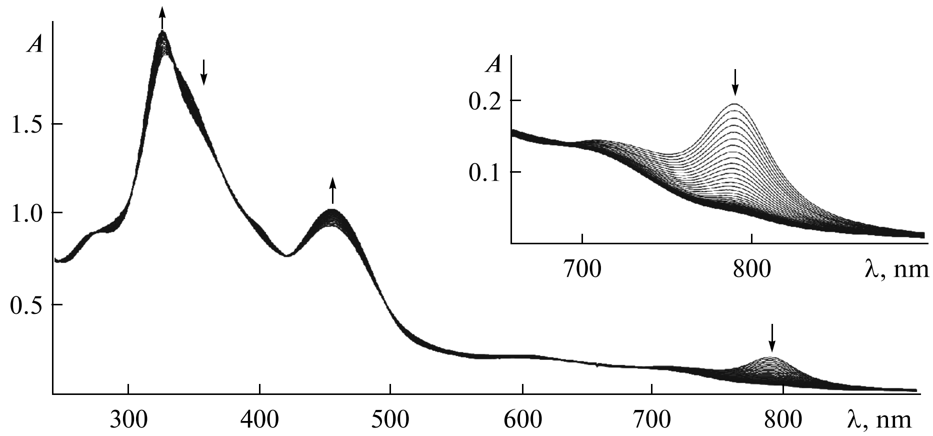


Fig. 7. Variation of the UV-Vis spectra of compound **2** in 17.77 M H_2SO_4 at 298 K and at time τ (s) varying from 0 to 100.

spectrum of free H_2OEP (four bands in the visible region plus the Soret band), thus confirming the absence of dissociation of the complex at the M–N bond. It corresponds to the species containing the hydrogen sulfate ion $O{=}Re(HSO_4)OEP$, as follows from comparison with the spectrum of $O{=}Re(HSO_4)^{5,15}DPOEP$ recorded under the same conditions (Fig. 6). Apparently, the hydrogen sulfate axial complex is formed under drastic conditions of recrystallization (temperature rise on mixing of H_2SO_4 and H_2O).

In terms of the stability against oxidation, the rhenium(V) porphyrin complexes are arranged in the series:

$$O{=}Re(OPh)OEP\ (\mathbf{1})^*,\quad O{=}Re(Cl)OEP\ (\mathbf{2})^*,$$
$$O{=}Re(OPh)MPOEP\ [27]^* > [O{=}ReTPP]_2O^{**}\ [14]$$
$$> O{=}Re(Cl)^{5,15}DPOEP\ (\mathbf{3}) \qquad (9)$$
$$(k^{298} = 2 \times 10^{-9}\ \mathrm{mol^{-1}\ L\ s^{-1}}) > O{=}Re(Cl)MPOEP$$
$$(k^{298} = 5 \times 10^{-8}\ \mathrm{mol^{-1}\ L\ s^{-1}}\ [27])$$

Compounds of this series have a same-type structure of the coordination unit but different types of the out-of-plane deformation of the substituted macrocycle (similar to copper(II) complexes [28]). The natures of the electronic effects of axial ligands and peripheral substituents are also different. It can be seen that only compounds that can be transformed into hydrogen sulfate axial complexes are oxidized. These include compounds with electron-withdrawing *meso*-phenyl substituents and axial chloride ion. This provides important conclusions. First, the arrangement of the complexes in series (9) is in agreement with the proposed scheme of MP transformations in sulfuric acid (reactions (4)–(7)). Second, the out-of-plane deformation of the macrocycle, which increases for diphenyl- and, the more so, tetraphenyl-substituted complexes [28], does not predominate over electronic factors. The complex O=Re(Cl)MPOEP devoid of this type of distortion is the last in the oxidation stability series. Owing to the positive inductive and mesomeric effects of the β-octaethyl substitution, complex **2**, despite the presence of the axial chloride ion, coordinates so strongly the macrocyclic ligand that attachment of the hydrogen sulfate ion as the *cis*-ligand becomes impossible.

The presented data demonstrate high reactivity of rhenium(V) porphyrins upon the replacement of axial ligands and formation of stable π-radical cations during oxidation processes. Both these factors are most important for the catalytic activity of MP, therefore, the results of this study will find use in consideration of metal porphyrins as catalysts.

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* Stable against oxidation.

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