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> LETTERS TO THE EDITOR

A First Example of Oxidation of Manganese(III) Porphyrin in Sulfuric Acid Solutions

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We studied spectrophotometrically the state and reactions of the Mn(III) complex with 2,7,12,17-tetramethyl-3,8,13,18-tetra(n-butyl)porphine [(Cl)MnP] (I) in acid solutions. The spectrum of I in acetic acid (AcOH) is similar to that in toluene, which indicates that the Mn(III) complex is stable in AcOH. However, its spectrum in concentrated H_2SO_4 [λ_{max} , nm (log ϵ): 427 (5.03), 571 (3.93), 620 (3.82), 768 (3.79)] differs essentially from the known spectra of porphyrins and their Mn(III) complexes in acids. In the mixed solvent AcOH-H₂SO₄ at 233-253 K, the electronic absorption spectrum of I changes with time: The characteristic bands of manganese(III) porphyrin decrease and disappear, and a very strong band appears with λ_{max} 429 nm. The spectrum evolution in characterized by well-defined isobestic points. After the process completion, the spectrum becomes identical to that in concentrated aqueous sulfuric acid. Such a pattern is observed with a Mn(III) porphyrin for the first time. The apparent rate constants of the process, calculated with a first-order equation, nonlinearly grow with an increase in the initial concentration of sulfuric acid in acetic acid. The negative logarithm of the rate constant at 25°C linearly correlates with the acidity function of the mixed solvent H_0 [1]. The slope of the straight line in these coordinates is close to 2, i.e., the experimental rate equation involves the total solution acidity squared:

$$-dC_{\mathbf{I}}/d\tau = kC_{\mathbf{I}}h_0^2,$$

where k is the rate constant; C_{I} , concentration of complex I; and h_0 , acidity of the medium.

The ESR spectra of sulfuric acid solutions of I at

143 K exhibit a characteristic signal of manganese with a hyperfine structure (g 2.007, A 9.8 mT). This fact indicates that the oxidation state of the central atom changed upon dissolution in acids, because for Mn(III) porphyrins, as well as for other systems with the high-spin d^4 electronic configuration, recording of the ESR spectra is impossible [2].

The product with λ_{max} 427–429 nm (II) is stable in the mixed solvent AcOH–H₂SO₄ and in concentrated H₂SO₄ in the cold for a long time (more than 3 months) and under heating. By reprecipitation from H₂SO₄ onto ice, we isolated the Mn(III) porphyrin. When complex I is dissolved in deaerated sulfuric acid, the spectral pattern is different, and product II is not formed.

Analysis of our results and published data [3] shows that compound **II** is an oxo complex (O)Mn^{IV}P formed by one-electron oxidation of the central manganese atom with oxygen in the presence of solvated protons.

The increase in the manganese oxidation state in porphyrin complexes in the presence of oxidants is a well-known phenomenon [3], but in strong acids the formation of a Mn(IV) complex is observed for the first time. All the previously studied Mn(III) complexes with porphyrins containing various substituents in β and *meso* positions of the macroring dissociate in concentrated sulfuric acid and its acetic acid solutions with the cleavage of metal–nitrogen bonds and release of the metal-free porphyrin in the diprotonated form [4].

Thus, in this study we found the first Mn(III) por-



Scheme of the synthesis of 2,7,12,17-tetramethyl-3,8,13,18-tetra(*n*-butyl)porphine **X**.

phyrin capable of oxidation to (oxo)manganese(IV) porphyrin in sulfuric acid solutions.

2,7,12,17-Tetramethyl-3,8,13,18-tetra(*n*-butyl)porphine (IX) was prepared as shown in the scheme, by the condensation of 3-butyl-2,4-dimethylpyrrole VI under the action of bromine in acetic acid to a mixture of dipyrrolylmethenes **VII** and **VIII**, followed by their reaction in formic acid similarly to [5]. Pyrrole VI was prepared by decarboxylation of 2-ethoxycarbonyl-4-butyl-3,5-dimethylpyrrole V under the action of KOH in ethylene glycol [6]. Pyrrole V, in turn, was prepared by Knorr condensation of alkylated acetylacetone III with nitrosated ethyl acetoacetate IV in acetic acid in the presence of zinc dust [7]. Yield of IX 18% based on pyrrole VIII. R_f (Silufol): 0.49 (benzene-heptane, 1:1). Electronic absorption spectrum (CHCl₃), λ_{max} , nm (log ϵ): 621 (3.77), 568 (3.87), 535 (4.05), 500 (4.17), 401 (5.26). ¹H NMR (CDCl₃, internal reference HMDS), δ, ppm: 10.06 s (4H, meso-H), 4.06 t (8H, CH₂C3H7), 3.62 s (12H, CH₃), 2.30 quintet (8H, CH₂CH₂C₂H₅), 1.81 sextet [8H, (CH₂)₂CH₂CH₃], 1.16 t (8H, CH₃-Bu), -3.80 br.s (2H, NH).

[2,7,12,17-Tetramethyl-3,8,13,18-tetra(*n*-butyl)porphinato]chloromanganese (I) was prepared by the reaction of porphyrin IX (0.5 mmol) with $MnCl_2 \cdot 4H_2O$ of analytically pure grade (2.5 mmol) in refluxing DMF (50 ml) for 20 min, isolated from the reaction mixture by extraction with chloroform, and purified by repeated washing of the chloroform solution with water followed by twofold chromatography on a column packed with Al₂O₃ (Brockmann grade II). Electronic absorption spectrum (toluene), λ_{max} , nm (log ε): 366 (4.63), 479 (4.53), 572 (3.83), 618 (shoulder); (AcOH): 375 (4.60), 474 (4.38), 559 (3.87), 601 (shoulder). R_f (Alufol, CHCl₃–1% C₂H₅OH) 0.35. IR spectrum (KBr), cm⁻¹: 2962, 2928, 2863, 2853 (v_{C-H}), 1445, 1364 (δ_{C-H}), 985, 955 (alkyl groups); 1646, 1274, 1152, 1105 (skeleton vibrations of pyrrole rings and macroring); 841 (γ_{C-H}) (vibrations of C–H in *meso*-positions); 1037 ($\delta_{C_{\beta}-C}$), 749 ($\gamma_{C_{\beta}-C}$) (vibrations of C–C bonds in γ -positions of the macroring).

The electronic absorption spectra were recorded on a Hitachi U-2001 spectrophotometer equipped with a temperature-controlled cell compartment. The ¹H NMR spectrum was taken on a Bruker spectrometer (200 MHz, reference HMDS). The IR spectrum was measured on an Avatar 360 FT-IR device from a KBr pellet. The ESR spectra in the digital form were recorded by A.V. Kulikov (Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia) with an SE/X 2544 3-cm ESR spectrometer (Radiopan, Poland) equipped with a magnetometer, a frequency meter, and a temperature unit.

Acetic acid solutions of H_2SO_4 of required concentrations were prepared gravimetrically from sulfuric acid (monohydrate) and chemically pure grade acetic acid dehydrated by stepwise thawing. Sulfuric acid (monohydrate) was prepared from 60% oleum and chemically pure grade H_2SO_4 with conductometric

monitoring. The oxidation rate was determined spectrophotometrically.

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