2. V. F. Mironov, E. N. Ofitserov, I. V. Konovalova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2118 (1990).
3. V. F. Mironov, T. N. Sinyashina, E. N. Ofitserov, et al., Zh. Obshch. Khim., 60, No. 4, 960 (1990).
4. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, et al., Topics in Phosphorus Chemistry, Vol. 5, Interscience Publishers, New York–London–Sydney (1967).
5. J. March, Organic Chemistry [Russian translation], Vol 1, Mir, Moscow (1987), p. 216.
6. H. R. Hudson, Topics in Phosphorus Chemistry, Vol. 11, New York–London–Sydney–Toronto, Interscience Publishers (1983), p. 340.
7. G. M. Kosolapoff and L. Maier, Organic Phosphorus Compounds, Vol. 6, J. Wiley & Sons, New York (1983).

ELECTROCHEMICAL REDUCTION OF Fe(III), Cr(III), AND Mn(III) PORPHYRIN COMPLEXES IN DMSO

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The half-wave potentials are given for the electrochemical reduction of Fe(III), Cr(III), and Mn(III) porphyrin complexes. Cyclic voltamperometry was used to study the reversibility of these reactions. An effect was demonstrated for the structure of the porphyrin ligand on the half-wave potentials for the reduction of the Mn(III) complexes.

The reduced forms of metalloporphyrins are electron donors in biological and industrial catalysis. Electrochemical methods have been used to study the reactions leading to the formation of such compounds [1,2]. The possibility of monitoring the charge transferred is an advantage of the electrochemical method for the generation of reduced forms of the catalyst since the corresponding potential is applied on the working electrode for obtaining the required intermediate species. In the present study, the formation of various reduced forms of Fe(III), Cr(III), and Mn(III) porphyrin complexes was investigated by cyclic and differential pulse voltamperometry.

EXPERIMENTAL

The voltamperometric methods were carried out using the ESM-700 electrochemical system manufactured in the German Democratic Republic on a platinum electrode in a cell held at 25°C in a nitrogen atmosphere. A standard calomel electrode was used as the reference electrode and 0.1 M Et_4NClO_4 was used as the base electrolyte.

The complexes were synthesized by the coordination of porphyrins with the corresponding metal acetates in DMF. The porphyrins were tetraphenylporphin (H_2TPP), tetra(pentafluoro)phenylporphin (H_2TPFPP), tetra(2-thienyl)porphin ($H_2TTP(2)$), tetra(5-amyl-2-thienyl)porphin ($H_2TATP(5,2)$), tetra(7-quinolinyl)porphin ($H_2TQP(7)$), and dimethyl ether of deuteroporphyrin (H_2DP, d.m.e).

RESULTS AND DISCUSSION

The reduction of these complexes in DMSO may be approximated by the following scheme:

$$M^{III}P^{+} + e \overset{1}{\rightleftarrows} M^{II}P + e \overset{2}{\rightleftarrows} M^{II}P^{-} + e \overset{3}{\rightleftarrows} M^{II}P^{2-} \qquad (1)$$

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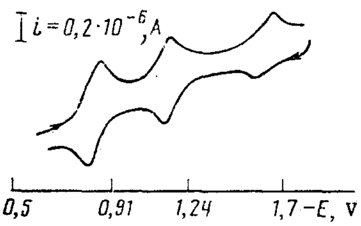


Fig. 1. Cyclic voltamperogram of a $5 \cdot 10^{-4}$ M solution of (Ac)CrTPP in DMSO with 0.1 M Et_4NClO_4.

The direction of the reduction of the metalloporphyrin (relative to the metal ion or ligand) was evaluated using the electrochemical criteria given by Enikolopyan [2]. Cyclic voltamperometry was used to show that the first two steps are one-electron, reversible processes for all the complexes ($\Delta E_e = 0.057$ V, $i_a/i_c = 1$ for $v = 0.05$ V/sec), while the third step for some metalloporphyrins such as $CrTPP^+$ and $MnTPP^+$ is only close to reversible ($\Delta E_e = 0.065$ V, $i_a/i_c = 0.9$). An example of a cyclic voltamperogram of $CrTPP^+$ is shown in Fig. 1. The (Ac)MP extracomplex in DMSO dissociates with the formation of the Ac^- acido ligand and MP^+ cation [3]. This cation is not shielded from a short-range interaction (specific solvation) with solvent molecules, which occupy coordination positions 5 and 6. Thus, the sequence of transformations (1) is rather tentative.

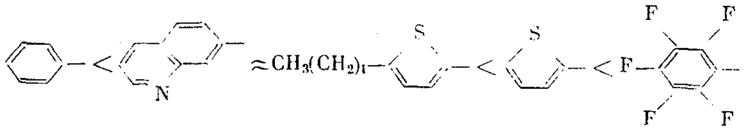
In the general case, the half-wave potentials ($E_{\frac{1}{2}}$), which are virtually the same as the standard oxidation–reduction potentials (E_0) for the reversible electron trans steps, characterize the reactivity of these compounds in redox reactions. Using values for E_0 and the following expression

$$\ln K = 2.3\,(E_0^{A} - E_0^{D})/RT, \tag{2}$$

the equilibrium constant in the homogeneous electron transfer from donor to acceptor may be evaluated [4]. Mairanovskii [5] has proposed the rather general nature of the inverse relationship between the electrochemical activity of the starting molecule (E_0) and chemical reactivity of the electron transfer product. The E_0 values of some metalloporphyrins correlate with the rate constants of their solvoprolytic dissociation [2].

Comparison of the E_0^1 ($E_{\frac{1}{2}}^1$) values of these complexes with the ionization potentials of the corresponding M(II) ions in the gas phase [6] showed the lack of a clear dependence between these terms. This behavior is probably due to nonuniform stabilization of the oxidation states of the various metal ions of the porphyrin ligand (different contributions of σ and π bonds) and change in the ΔG_s values in going from one redox pair to another (G_s is the standard free energy of solvation).

The $E_{\frac{1}{2}}$ value of the reduction wave of the metal ion within the complex depends on the structure of the porphyrin ligand.* For Mn(III) porphyrins, substituents in the meso positions of the porphyrin ring increase $E_{\frac{1}{2}}^1$ in the following series:



The substituent effect in the reduction of the porphyrin ligand ($E_{\frac{1}{2}}^2$) is evident to a greater extent. For $MnTPFPP^+$ and $MnTPP^+$, the difference in $E_{\frac{1}{2}}$ is 0.15 V in the first step and 0.35 V in the second step (Table 1).

Fuhrhop et al. [7] discovered a dependence between $E_{\frac{1}{2}}$ of metal octaethylporphyrin (H_2OEP) complexes which are reduced or oxidized in the ligand and the electronegativity of the metal. The dependence is given as follows for processes of their reduction

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*The concept that there is reduction of the metal ion is not always valid since the electron may occupy a mixed orbital.

TABLE 1. Reduction Half-Wave Potentials for Metalloporphyrins ($E_{1/2}$, V)

Compound	$-E^1_{1/2}$	$-E^2_{1/2}$	$-E^3_{1/2}$
$FeTPP^+$	0,11	1,16	1,68
$CrTPP^+$	0,91	1.24	1,70
$MnTPP^+$	0,25	1.23	1,76
$MnPFPP^+$	0,10	0,91	1,40
$MnTTP(2)^+$	0,16	1.11	1,58
$MnTATP(5,2)^+$	0,19	1,14	1,62
$MnTQP(7)^+$	0,20	1.18	1,58
$MnDP^+$ d.m.e.	0,28	1,51	–

$$E_{1/2}^{MP} - E_{1/2}^{H_2P} \simeq b(h_{ef} - 2.14), \tag{3}$$

where b = 0.23 and h_{ef} is the effective induction parameter, is equivalent to the electronegativity doubly-charged metals.

It has been assumed that the value of b would decrease somewhat in going from H_2OEP to more readily reduced porphyrins, e.g., coefficient b should depend on the structure of the porphyrin ligand [2]. The calculation carried out using Eq. (3) for Mn(II)P and the experimental data showed that the value of b in going from H_2DP, d.m.e. ($E_{1/2}$ = -1.29 V) to H_2TPP ($E_{1/2}$ = -1.08 V) indeed decreases by 0.054 unit, while this decrease in going to H_2T(pentafluoro)PP ($E_{1/2}$ = -0.74 V) is 0.068 unit.

LITERATURE CITED

1. B. D. Berezin and N. S. Enikolopyan, Metalloporphyrins [in Russian], Nauka, Moscow (1988), p. 97.
2. N. S. Enikolopyan (ed.), Spectroscopy, Electrochemistry, and Applications of Porphyrins [in Russian], Nauka, Moscow (1987), p. 127.
3. L. J. Boucher, Coord. Chem. Rev., 7, 289 (1972).
4. Z. V. Todres, Radical-Ions in Organic Synthesis [in Russian], Khimiya, Moscow (1988), p. 55.
5. V. G. Mairanovskii, Élektrokhimiya, 26, 443 (1990).
6. Chemist's Handbook [in Russian], Goskhimizdat, Moscow–Leningrad (1963), p. 325.
7. J. Fuhrhop, K. Kadish, and D. Davis, J. Am. Chem. Soc., 95, No. 16, 5140 (1973).