INTERACTION OF Mn(III)TETRAPHENYLPORPHYRIN WITH SUPEROXIDE; THE REACTION MECHANISM AND EVIDENCE FOR A PEROXO COMPLEX

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Cathodic one-electron reduction of Mn(III)TPP and O_2 in an aprotic solvent yields Mn(II)TPP and the superoxide anion radical O_2^-. The Mn(II)TPP and O_2^- react in solution to the side-on peroxo complex Mn(III)TPP–O_2^{2-}, which is oxidized at the electrode at a peak potential of E_{pa} = 0.40 V vs NHE ($k \approx 10^4\ dm^3\ mol^{-1}\ s^{-1}$). The rate-determining step of the overall two-electron oxidation is the transfer of the first electron coupled with a structure rearrangement of the peroxo complex to a superoxo complex.

The reactions of superoxide O_2^- with metal complexes are of considerable interest in connection with a number of important problems, such as the modelling of superoxide dismutases (SOD), the toxicity of oxygen (the formation of metal ions in unusually high oxidations states) and the preparation of dioxygen complexes.

The study of the interactions of manganese complexes with superoxide is motivated both by the existence of superoxide dismutase containing manganese and by the difficulties encountered in the preparation of dioxygen adducts of manganese via direct reaction with molecular oxygen[1]. It is known that the reactions of manganese(II) complexes with dioxygen are mostly irreversible; one of the first known complexes with dioxygen Mn(IV)TPP–O_2^{2-} (TPP = tetraphenylporphyrin) is stable at low temperatures (−78 °C) only[2,3].

VanAtta et al.[4] treated Mn(III)TPP with two equivalents of superoxide and obtained a crystalline product, characterized by X-ray crystallographic studies as the side-on peroxo complex Mn(III)TPP–O_2^{2-}. On the basis of electrochemical behaviour of manganese porphyrins in the presence of oxygen, the existence of Mn(II)–dioxygen intermediate has been postulated[5,6]. The reaction of Mn(III)TPP with dioxygen and the superoxide has been also studied by voltamperometric and spectroscopic methods[7]. The authors have suggested the formation of an end-on superoxo complex, which dimerizes to the mixed-valence μ-peroxo complex TPPMn(II)–O–O–Mn(III)TPP, at the end probably converted into a double-bridged μ-oxo complex.

In the present work we employed cyclic voltammetry to describe the individual oxidation–reduction steps and to characterize the intermediate in the reaction of Mn porphyrin with superoxide in a system containing Mn(III)TPP and O_2. The superoxide was generated electrochemically in situ to avoid alkalization of the solution by the addition of KO_2 which is always partially hydrolyzed. The traces of KOH can considerably distort the results due to uncontrolled generation of O_2^- catalyzed by traces of metals[8].

EXPERIMENTAL

Manganese(III)*meso*-tetraphenylporphyrin acetate, Mn(III)TPP (Strem Chemicals) and dimethyl sulfoxide, DMSO (Merck, p.a.) were used without further purification. Tetraethylammonium perchlorate (TEAP) was prepared by the reaction of tetraethylammonium chloride (Merck, p.a.) and perchloric acid (VEB Apolda, p.a.).

The voltammetric measurements were carried out in a three-electrode arrangement at a temperature of 22 °C. The indifferent electrolyte was TEAP ([TEAP] = 0.1 mol dm^{-3}) in DMSO. The required oxygen concentration was attained by introducing dry oxygen and nitrogen in a known ratio into the electrolyte in the vicinity of the working electrode. Peak current i_{pc} of O_2 reduction was used for evaluation of O_2 concentration; the calibration was based on the O_2 solubility in DMSO (2.20 . 10^{-3} mol dm^{-3}, ref.[9]).

The working electrode was a Pt wire (0.5 × 14 mm). A sodium amalgam $NaHg_x$ reference electrode was used; it was prepared by dissolving sodium in mercury. The potential of the reference electrode is 1.83 V more negative than that of the normal hydrogen electrode (NHE), as follows from the comparison of the half-wave potential $E_{1/2} = -0.53$ V vs NHE for the reduction of O_2 to O_2^- at a Pt electrode in DMSO (ref.[10]) with our measurements. The auxiliary Pt electrode was rectangular (10 × 7 mm) and was separated from the working electrode by sintered glass. The cyclic voltammograms were measured using a PA 4 analyzer (Laboratorni pristroje, Prague) and, at higher scan rates, using an EP21 potentiostat (ELPAN, Poland) with a computer fitted with an SHS AD unit.

Numerically differentiated voltammograms were treated using a program for convolution voltammetry[11] to yield curves analogous to the differential polarogram. Digital simulation of cyclic voltammograms based on solution of second Fick law by the method of finite differences taking into account homogeneous chemical processes[11], was used to model reactions in the presence of O_2^- and to estimate their rate constants.

The IR spectra were measured using a Specord M-80 grid spectrophotometer (Zeiss, Jena). Prior to and after saturation the solution with KO_2, the Mn(III)TPP sample was applied to the AgCl window (thickness 1 mm) and measured. The electronic absorption spectra of the samples were measured using a Philips PU 8700 UV/VIS spectrophotometer.

RESULTS

The electronic absorption spectrum of Mn(III)TPP is depicted in Fig. 1, curve *1* (λ_{max} = 377, 398, 466, 569 and 604 nm). Mn(II)TPP (Fig. 1, curve *2*) is formed by the reduction of Mn(III)TPP by potassium superoxide KO_2 in DMSO (ref.[12]) (λ_{max} = 397, 448, 574 and 617 nm).

In the absence of oxygen, the cyclic voltammogram of Mn(III)TPP (Fig. 2) consists of two reduction and two oxidation processes. The first reduction process corresponds to a one-electron reduction of the central ion characterized by the peak potential E_{pc} = 0.01 V vs NHE. Back oxidation of Mn(II)TPP to the initial Mn(III)TPP occurs on the anodic branch of the curve at a potential of 0.14 V vs NHE. The ratio of the anodic and cathodic peak currents $|i_{pa}/i_{pc}|$ is equal to 1 and $i_{pc}/v^{1/2}$ is independent of the scan rate up to the maximum rate used, 361 V s^{-1}. Thus, the reduction product Mn(II)TPP is stable in the electrolyte solution and does not undergo any chemical changes. The separation of the peak potentials $|E_{pa} - E_{pc}|$ is 0.13 V (at 0.1 V s^{-1}). The difference is greater than the value of 0.059 V for a reversible one-electron process. The electrode reaction is not perfectly reversible, as a consequence of complex rearrangement coupled with a change of the oxidation degree of manganese (the standard rate constant is 1 . 10^{-3} cm s^{-1} according to ref.[13]).

The second reduction process at a potential of –0.98 V vs NHE is the reduction of Mn(II)TPP to the $[Mn(II)TPP]^-$ anion radical. It follows from the ratio $|i_{pa}/i_{pc}| > 1$ and from its independence of the scan rate (0.05 – 0.2 V s^{-1}) that $[Mn(II)TPP]^-$ does not undergo further chemical reactions either. It is apparent from the difference $|E_{pa} - E_{pc}|$ = 0.06 V (for scan rates of 0.050 V s^{-1} and 0.1 V s^{-1}) that the electrode process is reversible.

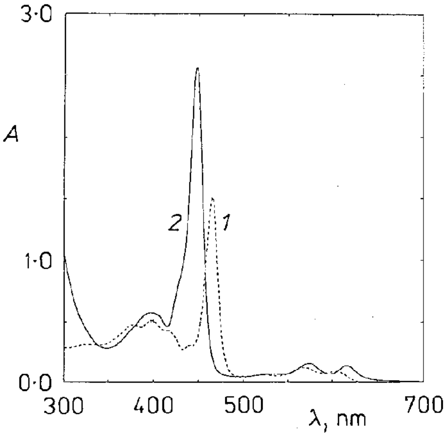


FIG. 1

Absorption spectra of manganese complex in DMSO. *1* Mn(III)TPP, [Mn(III)TPP] = 1 . 10^{-5} mol dm^{-3}; *2* Mn(II)TPP, [Mn(II)TPP = 1 . 10^{-5} mol dm^{-3}, $[O_2^-] \approx 3 . 10^{-4}$ mol dm^{-3}

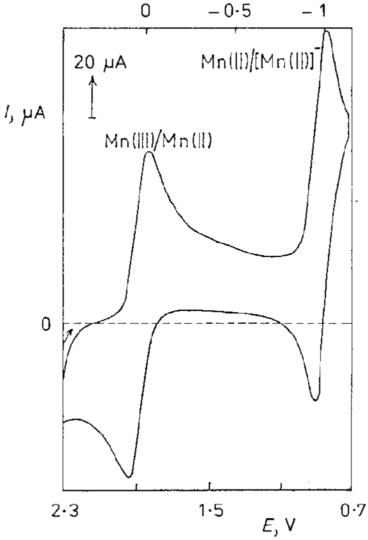


FIG. 2

Cyclic voltammogram of Mn(III)TPP. [TEAP] = 0.1 mol dm^{-3} in DMSO, 0.1 V s^{-1}, [Mn(III)TPP] = 8.6 . 10^{-4} mol dm^{-3}. Potentials: upper scale vs NHE, lower scale vs $NaHg_x$

This situation is changed after the introduction of oxygen into the electrolyte. Figure 3 displays the first measurement in the potential range 0.47 V to –0.31 V, where only oxidation and reduction of the central ion occur. The current ratio i_{pa}/i_{pc} is equal to 1, i.e. the reaction is diffusion-controlled. Consequently, the actual redox process is not affected by the presence of oxygen. Any direct reaction of Mn(II)TPP with oxygen is relatively slow and does not influence the measurement.

If the potential sweep continues to the potential of O_2^- formation, then the anodic branch of the voltammogram is greatly changed (Fig. 3). The anodic peak current of O_2^- is diminished, i.e. the ratio of the peak currents $i_{pa}/i_{pc} < 1$. It means that O_2^- formed at the electrode is consumed in a chemical reaction in solution. Mn(II)TPP is consumed in a homogeneous reaction as well, as its anodic peak current i_{pa} is much smaller than it corresponds to the i_{pc} value for Mn(III)TPP. Moreover, a new oxidation peak appears at a potential E_{pa} = 0.04 V vs NHE, corresponding to the product of the homogeneous reaction between Mn(II)TPP and O_2^-. The proportion of the peak currents for O_2 and Mn(III)TPP depends on the concentration of O_2. At the oxygen concentration as low as $[O_2] = 6.9 \cdot 10^{-4}$ mol dm^{-3} and scan rate of 0.1 V s^{-1}, the peak of Mn(II)TPP disappears entirely as all the Mn(II)TPP has been converted to the product.

The oxidation of the new product is electrochemically irreversible as no corresponding reduction process was observed. The anodic peak potential of the product shifts with increasing scan rate to more positive values (Fig. 4). Simultaneously, the peak current i_{pa} of the product decreases and the peak current of of Mn(II)TPP increases thus indicating lower degree of conversion in the homogeneous reaction due to shorter time

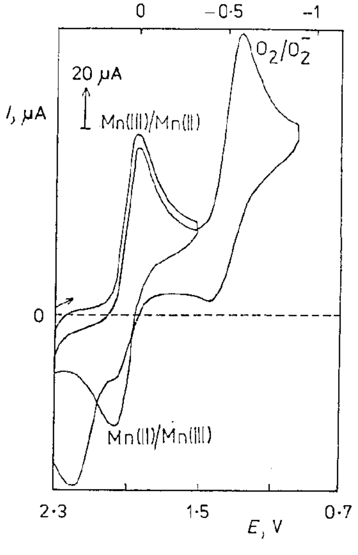


FIG. 3

Cyclic voltammogram of Mn(III)TPP in the presence of O_2. [TEAP] = 0.1 mol dm^{-3} in DMSO, 0.1 V s^{-1}, [Mn(III)TPP] = $6.5 \cdot 10^{-4}$ mol dm^{-3}, $[O_2] = 2.2 \cdot 10^{-4}$ mol dm^{-3}. Potentials: upper scale vs NHE, lower scale vs $NaHg_x$

available for the reaction at higher scan rate. The dependence of the proportion of the two processes on the scan rate is evident from the 1st derivative of the convolution voltammogram in Fig. 5.

After the addition of O_2^- to Mn(III)TPP, the IR spectrum shows a new vibrational band at 883 cm^{-1}, corresponding to the characteristic vibration ν(O–O) of the mononuclear peroxo complexes[1].

DISCUSSION

The reduction of Mn(III)TPP at the electrode yields Mn(II)TPP, which does not react with oxygen within the time interval in cyclic voltammetry (up to seconds), as it follows from the fact that the reduction and oxidation processes are not affected by the presence of O_2. It enables to study the reaction of Mn(II)TPP with superoxide in the presence of O_2 without the complication of irreversible oxidation of the complex. In general, the tetradental complexes of Mn(II) are irreversibly oxidized by oxygen[1] to yield Mn(III) or Mn(IV) complexes, usually in the form of μ-oxocomplexes[14 – 16]. The intermediates in these reactions are the corresponding hydroxo[16,17] or peroxo complexes[12,14].

Direct electron transfer between Mn(II)TPP and O_2 yielding the superoxide O_2^- according to Eq. (*A*)

$$\text{Mn(II)TPP} + O_2 \longrightarrow \text{Mn(III)TPP} + O_2^- \qquad (A)$$

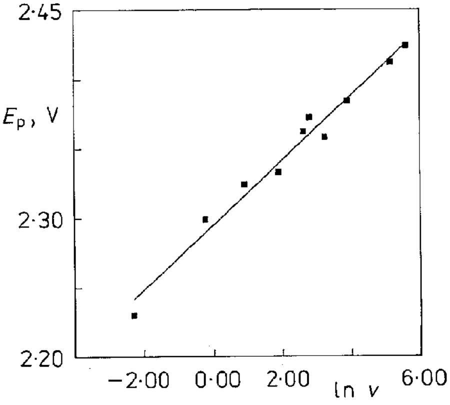


FIG. 4
The peak potential E_{pa} vs the logarithm of the scan rate *v* (V s^{-1}). The slope yields α n_a = 0.556. Potentials vs $NaHg_x$

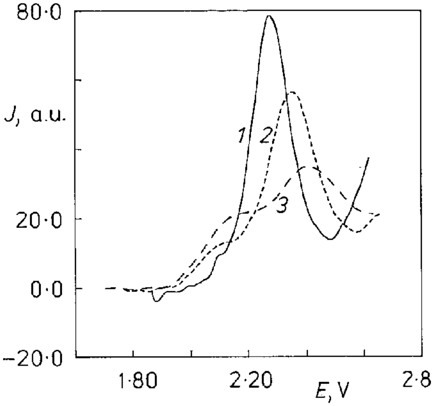


FIG. 5
First-order derivatives of the convolutive voltammograms. Scan rate: *1* 0.79 V s^{-1}; *2* 16.4 V s^{-1}; *3* 171.8 V s^{-1}. Potentials vs $NaHg_x$

can be excluded because the cathodic peak of O_2 lies at much more negative potentials than the cathodic peak of Mn(III)TPP.

At room temperature the formation of the dioxygen adduct Mn(IV)TPP–O_2^{2-} can also be excluded[2,3,18].

The amount of Mn(II)TPP is decreased by homogeneous reaction of Mn(II)TPP with O_2^- formed by the electrode reduction of O_2. This way a new product is generated and it is oxidized at the electrode at E_{pa} = 0.40 V vs NHE. The new product is apparently the peroxo complex Mn(III)TPP–O_2^{2-} (Eq. (*B*)), whose formation was postulated for the reaction of Mn(III)TPP with two equivalents of O_2^- (refs[7,12]). The characteristic vibration ν(O–O) = 883 cm^{-1} of the new product is in agreement with values for the side-on peroxo complexes[1,4]. As the cyclic voltammogram of Mn(III)TPP is not affected by the presence of oxygen, Mn(III)TPP–O_2^{2-} cannot be formed by the addition of O_2 to the reduced Mn(II)TPP and subsequent one-electron reduction (the ECE mechanism)[5,6]. The rate constant of reaction (*B*) is of the order of $k \approx 10^4\ dm^3\ mol^{-1}\ s^{-1}$.

$$\text{Mn(II)TPP} \quad + \quad O_2^- \xrightarrow{k} \text{Mn(III)TPP–}O_2^{2-} \qquad (B)$$

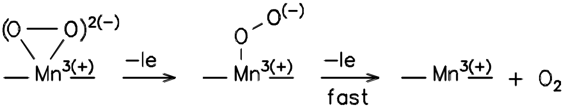
The peak current i_{pa} for the oxidation of Mn(III)TPP–O_2^{2-} (scan rate 0.05 – 0.2 V s^{-1}) is 1.6 to 1.9 times higher than the i_{pc} value for the reduction of Mn(III)TPP to Mn(II)TPP. The peak current i_{pa} (A) for an irreversible wave depends on the total number of electrons in the oxidation *n*, the diffusion coefficient D_0 ($cm^2\ s^{-1}$), the bulk concentration of the reduced species C_0 (mol cm^{-3}), the electrode area *A* (cm^2), the scan rate *v* (V s^{-1}), the transfer coefficient α and the number of electrons transferred in the rate-determining step n_a (Eq. (*1*), ref.[19])

$$i_p \quad = \quad (2.99\ .\ 10^5)\ n\ (\alpha\ n_a)^{1/2}\ A\ C_0\ D_0^{1/2}\ v^{1/2}\ . \qquad (1)$$

It can be expected that the mobility of Mn(III)TPP–O_2^{2-} will be lower as a consequence of interaction with the bulky cation of the supporting electrolyte than that of Mn(III)TPP, which has an overall charge of +1 only. The mobility of the ion u_i is directly proportional to the diffusion coefficient, $D \approx u_i$. Hence, the increase in the anodic current during the oxidation of the peroxo complex is due to the fact that Mn(III)TPP–O_2^{2-} is oxidized at the electrode in a two-electron process (Eq. (*C*)) and not to a change in the diffusion coefficient. The oxidation products are the initial Mn(III)TPP and O_2. Therefore, no corresponding reduction process is observed on the cathodic branch.

$$\text{Mn(III)TPP–}O_2^{2-} \xrightarrow{-2e} \text{Mn(III)TPP} \quad + \quad O_2 \qquad (C)$$

The peak potential E_{pa} of the irreversible wave is shifted to more positive potentials by $(1.15\ R\ T)/(\alpha\ n_a\ F)$ for each tenfold increase in v. Because $(\alpha\ n_a)$ is equal to 0.556 (Fig. 4) and the transfer coefficient α usually has a value of 0.3 to 0.7, then $n_a = 1$, i.e. the rate-determining step is a one-electron transfer, probably the transfer of the first electron, coupled with shortening of the O–O bond and with a change from the side-on "peroxide-like" to an end-on "superoxo-like" structure, Eq. (*D*).



(*D*)

The transfer of the second electron is fast. Both electrons are transferred to the dioxygen moiety.

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