

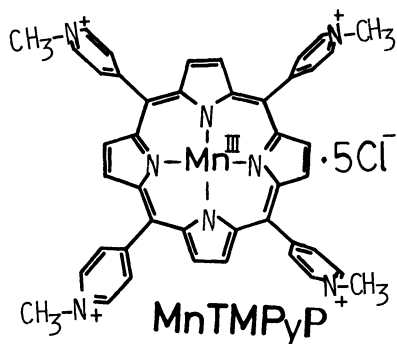
CATALYTIC ELECTROREDUCTION OF MOLECULAR OXYGEN USING [5,10,15,20-TETRAKIS-(1-METHYLPYRIDINIUM-4-YL)PORPHINATO]MANGANESE

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The water-soluble manganese porphyrin in the title was found to catalyze electroreduction of oxygen. The reaction could be explained by an electrochemical (EC) catalytic regeneration mechanism, and at the porphyrin concentrations of more than *ca.* 5×10^{-5} mol dm⁻³ two-electron reduction was attained. Electronic absorption and magnetic circular dichroism (MCD) spectroscopies have suggested that the active species of the porphyrin is in a high-spin divalent state.

The search for a relatively inexpensive catalyst/electrode combination for the electrochemical reduction of molecular oxygen (O₂) has received great interest for the last two decades. The metal macrocyclic compounds especially metal porphyrins and phthalocyanines have been frequently employed as potential catalysts.¹⁾ By the accumulation of results of about 50 papers, iron and cobalt complexes are known to show high catalytic activity. In this preliminary communication, we would like newly to report that a manganese porphyrin included in the title (MnTMPyP) also has high catalytic activity toward O₂ electroreduction.



MnTMPyP was prepared according to the general procedures as follows. 5,10,15,20-Tetrapyridyldorphine (TPyP) was reacted with excess MnSO₄ in refluxing *N,N*-dimethylformamide (DMF),²⁾ and after removal of the solvent the residue was imposed on a silica gel column to remove extra MnSO₄ (eluent, CHCl₃-MeOH (85:15 vol/vol)). The resultant MnTPyP was methylated with methyl *p*-toluenesulfonate in DMF³⁾ and the counter anion was exchanged to chloride by using Amberlite IRA-400 ion exchange resin.

Found: C, 55.65; H, 4.48; N, 11.73%. Calcd for Mn₁C₄₄H₃₆N₈Cl₅(H₂O)₂: C, 55.92; H, 4.27; N, 11.86%. Thus obtained MnTMPyP showed high solubility in water below pH 0 to above 14 (however, a gradual demetallation from Mn^{II}TMPyP was recognized spectrophotometrically at pH < *ca.* 3.5).⁴⁾

Figure 1 trace A shows cyclic voltammogram (*i* - *E* curve) at a glassy carbon (GC) electrode⁵⁾ for a homogeneously dissolved Mn^{III}TMPyP. The redox couple at -0.19 V was independent of the scan rate, *v*, from 10 to 200 mV s⁻¹ and the separation between the cathodic and anodic peak potentials, Δ*E*_p, was 62-74 mV, indicating one-electron transfer reaction. Also *i*_{p,c} (cathodic peak current) and *i*_{p,a} (anodic peak current) were linearly proportional to *v*^{1/2}, as expected from a diffusion-controlled process. As will be substantiated in Fig. 4, this redox couple is that of manganese(III/II)

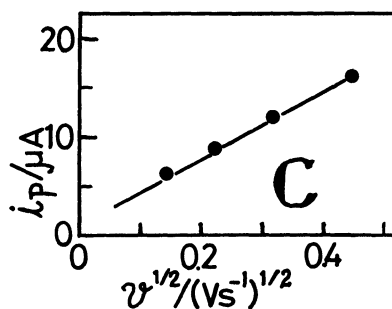
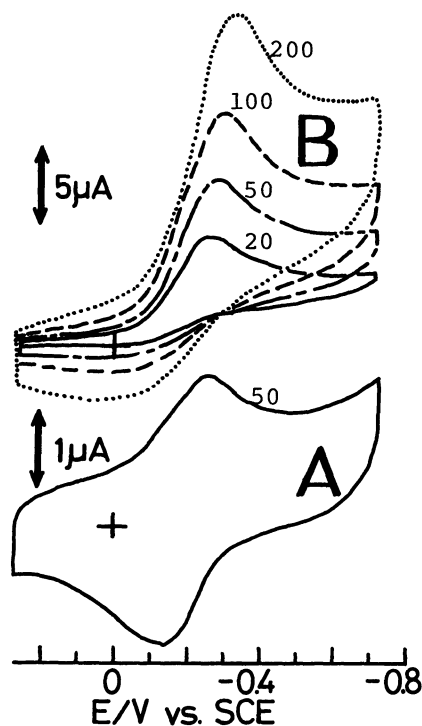


Fig.1. Cyclic voltammetric i - E curves for (A) N_2 saturated 2.6×10^{-4} M $Mn^{III}TMPyP$, (B) 2.4×10^{-4} M O_2 and 6.5×10^{-5} M $Mn^{III}TMPyP$. Numbers indicate scan rate in $mV s^{-1}$. GC electrode area/ $cm^2 = 0.08$. Solvent = 0.1 M phosphate buffer, pH 7. Trace C shows O_2 reduction peak current replotted from B as a function of $v^{1/2}$. (1 M = 1 mol dm^{-3}).

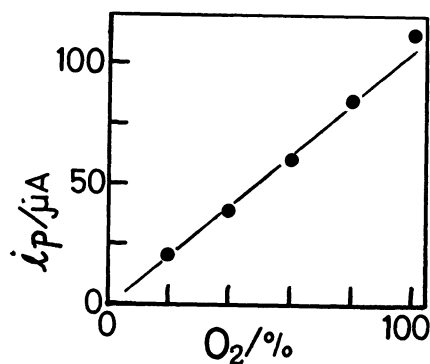


Fig.2. The effect of O_2 concentration on the reduction peak current for the 0.1 M Tris buffer (pH 9.0) containing 5.7×10^{-5} M $Mn^{III}TMPyP$. Scan rate was fixed at $50 mV s^{-1}$.

and was pH independent between pH 3.5 and 9.

When air (oxygen) was admitted into this solution ($C_{O_2} = 2.4 \times 10^{-4}$ M (1 M = 1 mol dm^{-3})),³⁾ Fig. 1 trace B was recorded. In order to obtain this trace, the $MnTMPyP$ concentrations of more than $ca. 5 \times 10^{-5}$ M was required. The reduction of O_2 occurred at $ca. -580$ mV vs. a saturated calomel electrode (SCE) in the absence of catalyst.⁶⁾ Accordingly, the use of $MnTMPyP$ as a catalyst lessens the overpotential by $ca. 350$ mV. The O_2 reduction potential in the presence of $MnTMPyP$ accorded with the reduction potential of Mn^{III} - to Mn^{II} - $TMPyP$ and was pH independent between pH 3.5 and 9, precluding the participation of protons or hydroxyl anions in this pH region. The i_p value for O_2 reduction was proportional to O_2 concentration in solution (Fig. 2) at a fixed scan rate and also linear as function of $v^{1/2}$ when the O_2 concentration was held constant.

Assuming an O_2 diffusion coefficient value of $2.1 \times 10^{-5} cm^2 s^{-1}$,^{1,2,3)} the slope of i_p versus $v^{1/2}$ plots gave an n value of 1.9 ± 0.1 , suggesting that H_2O_2 is the major product of oxygen reduction. i - E Curves similar to trace B in Fig. 1 were obtained at $MnTMPyP$ adsorbed electrode also, if the GC electrode was soaked in >1 mM $MnTMPyP$ solution for more than 10 min, rinsed carefully with distilled water, and then replaced to air-saturated solution devoid of catalyst. However, after 15 to 17 times of potential sweeps between $+0.3$ V

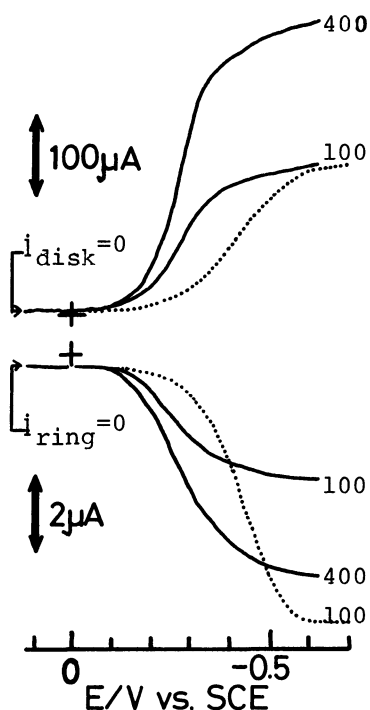
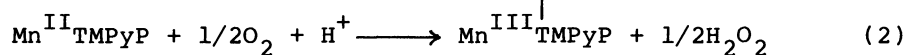


Fig. 3. Rotating ring-disk i - E curves for pure O_2 saturated $0.1\text{ M KH}_2\text{PO}_4$ (adjusted to pH 7 by NaOH) solution containing $1.5 \times 10^{-4}\text{ M MnTMPyP}$ (—) and in the absence of the catalyst (.....). The ring potential/ $V = +0.7$ vs. SCE. Disk electrode area/ $\text{cm}^2 = 0.22$. Numbers indicate rotation speed in rpm.

absorption peak disappeared and the Soret peak appeared at 441 nm, and two Faraday A terms in $\text{Mn}^{\text{III}}\text{TMPyP}$ disappeared to produce only one Faraday A term. When O_2 was introduced to $\text{Mn}^{\text{II}}\text{TMPyP}$ solution, the spectra returned immediately to those of $\text{Mn}^{\text{III}}\text{TMPyP}$. Thus the active species of MnTMPyP is a high-spin manganese(II) complex.

From the results mentioned above, the most plausible mechanism appears to be an EC catalytic regeneration mechanism (Eqs. 1 and 2).



The rate constants for Eqs. 1 and 2 were determined from the ΔE_p dependence of $\text{Mn}^{\text{III/II}}\text{TMPyP}$ redox couple on the scan rate¹¹⁾ and from the intercept of Koutecky-

and -0.8 V , the activity of the MnTMPyP adsorbed electrode disappeared. This short durability is a common aspect for cobalt or iron porphyrin or phthalocyanine immobilized electrodes⁷⁾ and may be due to the decomposition by hydrogen peroxide produced.

Figure 3 represents ring(platinum)-disk(GC) responses for O_2 reduction in pure O_2 saturated solution ($C_{O_2} = 1.1\text{ mM}$ ^{1,8)}) in the presence of MnTMPyP . When the disk electrode potential reached ca. -0.4 V , the amount of the current matched approximately that expected from the Levich equation⁹⁾ for a two-electron reduction of oxygen. The ring electrode potential was, on the other hand, set at $+0.7\text{ V vs. SCE}$ ⁶⁾ to detect H_2O_2 . As Fig. 3 reveals, H_2O_2 production commenced at the potential where O_2 reduction occurred and increased with the increase of disk potential, and at ca. -0.4 V where the disk current attained two-electron reduction of O_2 , it was saturated. Thus the results of Fig. 3 also show that H_2O_2 is the major reduction product.^{1,8)}

Figure 4 shows electronic absorption and MCD spectra of MnTMPyP in the absence and presence of applied potential (-0.4 V). In the absence of an applied potential, MnTMPyP displayed the red-shifted Soret band at 462 nm and a weak near-IR band at 770 nm characteristic of high-spin Mn^{III} porphyrins.¹⁰⁾ The MCD spectrum of this species consists of two Faraday A term type curves in the Soret region and a broad seemingly B term type curve in the visible region. When -0.4 V was applied to $\text{Mn}^{\text{III}}\text{TMPyP}$ in an optically transparent thin layer electrode (OTTLE) which contained a platinum minigrid as the working electrode, the spectra changed dramatically especially in the Soret region and finally became those of Mn^{II} high-spin porphyrins.¹⁰⁾ Namely, the near-IR ab-

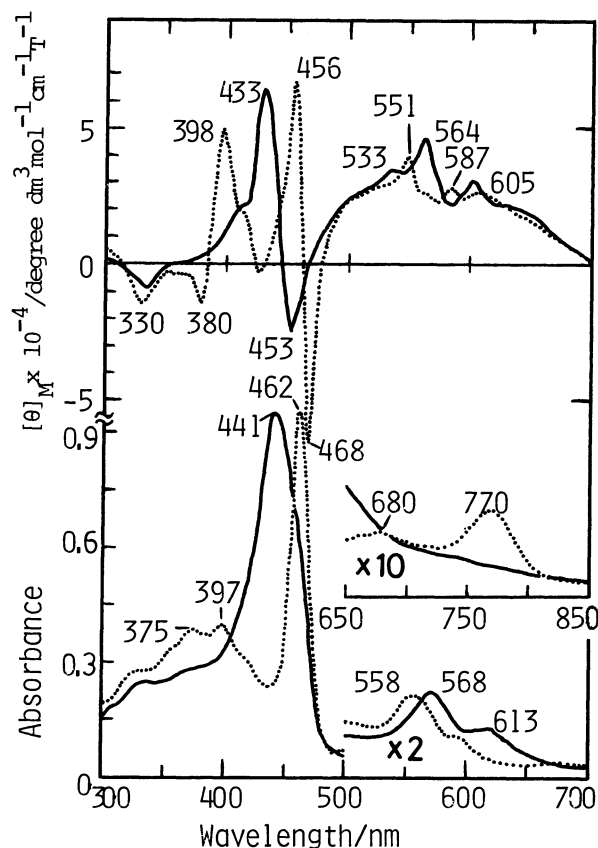


Fig. 4. UV-visible absorption (bottom) and MCD (top) spectra of $\text{Mn}^{\text{III}}\text{TMPyP}$ (.....) and electrogenerated (applied potential/ $V = -0.4$ V vs. SCE) $\text{Mn}^{\text{II}}\text{TMPyP}$ (—) in 1 M Na_2SO_4 plus 0.1 M KH_2PO_4 plus trace amount of NaOH (pH 6.5). Pathlength of the OPTLE/mm = 1.0. $[\text{MnTMPyP}/M] = 0.1$ mM. Field/ $T = 1.1$.

Levich plots^{1,9,12)} replotted from the data of rotating ring-disk experiments to be *ca.* 2×10^{-3} cm s^{-1} and 1.1×10^6 $\text{M}^{-1}\text{s}^{-1}$, respectively.

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