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SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF THE OXIDATION OF *PARA*-SUBSTITUTED TETRAPHENYLPORPHINATO MANGANESE (II) COMPLEXES

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SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF THE OXIDATION OF PARA-SUBSTITUTED TETRAPHENYLPORPHINATOMANGANESE (II) COMPLEXES

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The reaction of dioxygen with a series of *para*-substituted *meso*-tetraphenylporphinat manganese (II) complexes, $\text{Mn}^{\text{II}}(\text{T}(p\text{-x})\text{PP})(\text{BuNH}_2)$ where $x = \text{H}, \text{CH}_3, \text{Cl}, \text{OCH}_3$ in chloroform was studied. Oxidation rate constants were determined at room temperature using spectrophotometric methods. Fitting the observed values for the autoxidation rate constants to the Hammett equation ($\log k_b$ vs 4σ) gave a Hammett ρ_b value of -0.280 . The effect of substituents upon the *pseudo*-first-order rate constants is discussed. In comparison, the half-wave potentials ($E_{1/2}$) for the metal centred redox reaction, $[\text{Mn}^{\text{II}}(\text{T}(p\text{-x})\text{PP})(\text{BuNH}_2)] \rightleftharpoons [\text{Mn}^{\text{III}}(\text{T}(p\text{-x})\text{PP})(\text{BuNH}_2)]^+ + e$, were investigated by cyclic voltammetry. A relationship between $E_{1/2}$ and the Hammett constants was found.

Keywords: Manganese; porphyrin; oxidation; kinetics; electrochemistry

INTRODUCTION

There is growing interest in manganese porphyrin complexes because of their obvious relevance as biological models. Basolo and coworkers showed that *meso*-tetraphenylporphinat manganese(II) complexes $\text{Mn}^{\text{II}}(\text{TPP})(\text{L})$, where L represents a coordinating ligand, reversibly bind oxygen in toluene solution at 195K.¹ At room temperature, the complexes are oxygen sensitive.²

Molecular oxygen is a strong thermodynamic oxidant but reacts only slowly with many available reducing agents in the natural environment. Much effort

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has gone into understanding synthetic and natural catalysts that promote the reaction of dioxygen with oxidizable substrates. In this paper we first present the oxidation rate constants of a series of *para*-substituted $\text{Mn}^{\text{II}}(\text{T}(p\text{-x})\text{PP})(^n\text{BuNH}_2)$ complexes with dioxygen at room temperature. Because of the conjugated nature of the porphyrin ring system, electron donating or withdrawing substituents on the periphery of the molecule have been shown to affect the basicity of the porphyrin nitrogens.⁴⁻⁵ This in turn often affects the reactions and other physical properties of metalloporphyrins. We have observed that the Hammett constants, 4σ , of the *para* substituents of the four phenyl groups of the manganese porphyrin are related to the oxidation rate constants and the half-wave potentials for metal redox reactions.

EXPERIMENTAL

Reagents

n-Butylamine was refluxed with solid KOH for 10 hours and distilled under an N_2 atmosphere. Chloroform was distilled from P_2O_5 . Supporting electrolyte tetrabutylammonium perchlorate. TBAP was prepared from tetra-butylammonium bromide and perchloric acid and was recrystallized three times from ethyl acetate and vacuum dried for 24 hours prior to use. All other reagents were of A. R. grade and were used without further purification.

Synthesis

The compounds $\text{T}(p\text{-x})\text{PPH}_2$ and $\text{Mn}^{\text{III}}(\text{T}(p\text{-x})\text{PP})\text{Cl}$ were prepared by the method of Adler and co-workers.⁵⁻⁶ $\text{Mn}^{\text{II}}(\text{T}(p\text{-x})\text{PP})(^n\text{BuNH}_2)$ species were synthesized by the NaBH_4 reduction method.⁷ Satisfactory elemental analyses were obtained and electronic and IR spectra corresponded with literature data.

Rate Constants Measurement

Ultraviolet and visible absorption were measured at $292 \pm 1\text{K}$ using a Shimadzu UV-240 spectrophotometer. In all cases, the rate constants (k_{obs}) were measured in a chloroform solution of $\text{Mn}^{\text{II}}(\text{T}(p\text{-x})\text{PP})(^n\text{BuNH}_2)$, which was saturated with dioxygen and contained varying amounts (2%~10% v/v) of the ligand $^n\text{BuNH}_2$. Starting porphyrin concentrations were in the range 10^{-6} ~ $10^{-5}\text{mol dm}^{-3}$. All spectra were obtained in a capped quartz cell with a light path of 10mm.

Cyclic Voltammetry

Cyclic voltammograms were obtained using a BAS-100B electrochemical analyzer. A three-electrode system was used, consisting of a glassy-carbon working electrode, a platinum-wire auxiliary electrode and a commercial saturated calomel reference electrode (SCE), separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solution in the bridge was changed periodically to avoid aqueous contamination from entering the cell *via* the SCE. Deaeration was accomplished by passing high purity argon through the solution for 10 min and blanketing the solution during analysis.

$E_{1/2}$ values were measured as that potential lying midway between the oxidation and reduction peak for a given couple. All experiments were carried out at 293 ± 1 K and potentials are reported with respect to SCE.

RESULTS

The autoxidation reactions were monitored spectrophotometrically at 440 and 470 nm. Typical spectra are shown in Figure 1.

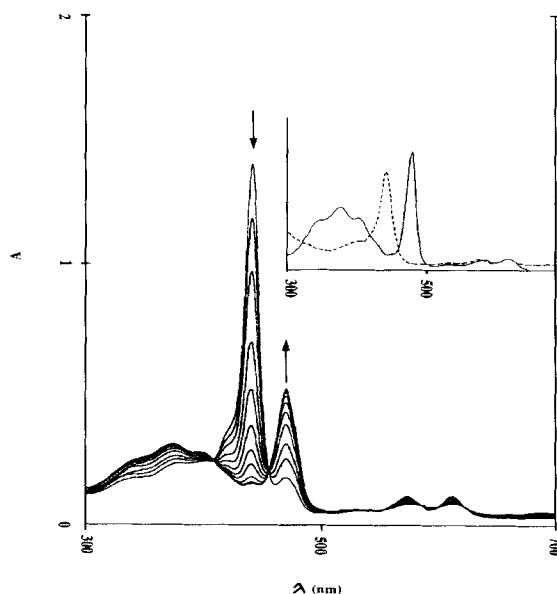


FIGURE 1 Change in absorbance with time for $\text{Mn}(\text{TPP}) (\text{}^t\text{BuNH}_2)$ at 292K in CHCl_3 solution containing 10%V/V $\text{}^t\text{BuNH}_2$. The arrows indicate the progression of the reaction. (inset) Absorption spectra of $\text{Mn}(\text{II})(\text{TPP}) (\text{}^t\text{BuNH}_2)$ and $\text{MnTPP}(\text{III})\text{Cl}$ (solid and dashed lines, respectively).

By comparing spectra of $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})(^n\text{BuNH}_2)$ and $\text{Mn}^{\text{III}}(\text{T}(p-x)\text{PP})\text{Cl}$, it is clear that the absorbance change at 440 and 470 nm in Figure 1 represents the oxidation of $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})(^n\text{BuNH}_2)$ to $\text{Mn}^{\text{III}}(\text{T}(p-x)\text{PP})^+$. Data from the spectra were fitted to equations (1) and (2),

$$\text{Ln}A_{440} = -k_{\text{obs}}t + \text{Ln}C\epsilon_{440} \quad (1)$$

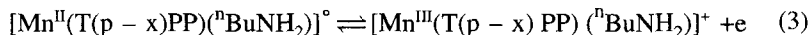
$$\text{Ln}(A_{\infty} - A)_{470} = -k_{\text{obs}}t + \text{Ln}C\epsilon_{470} \quad (2)$$

where k_{obs} and ϵ represent the *pseudo*-first-order rate constant and molar absorption coefficient, respectively, C represents the starting concentration of $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})(^n\text{BuNH}_2)$, A is the absorbance at time t and A_{∞} is the maximum equilibrium absorbance. At 440 and 470 nm, the plot of $\text{Ln}A$ vs t gave a straight line with good correlation coefficient ($r > 0.99$). At 470 nm, because of the difficulty in obtaining A_{∞} , we used computer simulation of the process to obtain k_{obs} (Table I). The k_{obs} values for each compound obtained from absorbance changes at 440 and 470 nm are in good agreement.

TABLE I *Pseudo*-first-order rate constants for reactions described at 293K

X	440nm		470nm	
	$k_{\text{obs}}(s^{-1})$	r	$k_{\text{obs}}(s^{-1})$	r
OCH ₃	7.83×10^{-4}	-0.997	7.81×10^{-4}	-0.996
CH ₃	4.44×10^{-4}	-0.992	4.48×10^{-4}	-0.998
H	3.17×10^{-4}	-0.991	3.25×10^{-4}	-0.994
Cl	6.98×10^{-5}	-0.9097	6.81×10^{-5}	-0.991

The electrochemical reaction investigated in this paper is given in equation (3).



As seen from Table II, the ratio of oxidation to reduction peak currents ($i_{\text{pa}}/i_{\text{pc}}$) is near unity and the separation between oxidation and reduction peak potentials (ΔE_p) is about 100mV. These results correspond to a diffusion controlled, one-electron, metal-centred oxidation process.⁸

TABLE II Cyclic voltametric data for the reactions described at 293K

X	4σ	$E_{1/2}/V$	$\Delta E_p/mV$	$i_{\text{pa}}/i_{\text{pc}}$
OCH ₃	-1.08	-0.247	96	0.92
CH ₃	-0.68	-0.243	101	0.96
H	0.00	-0.224	96	1.00
Cl	0.92	-0.185	96	0.90

DISCUSSION

Mechanism

The good isobestic behaviour and correlation coefficient (r) of LnA_{440} vs t and $\text{Ln}(A_{\infty}-A)_{470}$ vs t from our experiment confirm that the oxidation of $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})(^n\text{BuNH}_2)$ to $\text{Mn}^{\text{III}}(\text{T}(p-x)\text{PP})^+$ is a *pseudo*-first-order reaction and the rate constant is independent of the starting concentration of $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})(^n\text{BuNH}_2)$. Bosolo¹⁰ and others¹¹ showed that the reaction product of dioxygen with divalent manganese porphyrin is formulated as an Mn (III)-superoxide adduct and there is no ligand occupying the vacant axial position. Dependence of k_{obs} on the concentration of axial ligand $^n\text{BuNH}_2$ is shown in Figure 2. Increasing concentration of $^n\text{BuNH}_2$ causes a decrease of the k_{obs} value. The presence of axially bound *n*-butylamine is seen to inhibit the reaction competitively. We propose the oxidation mechanism as given below.

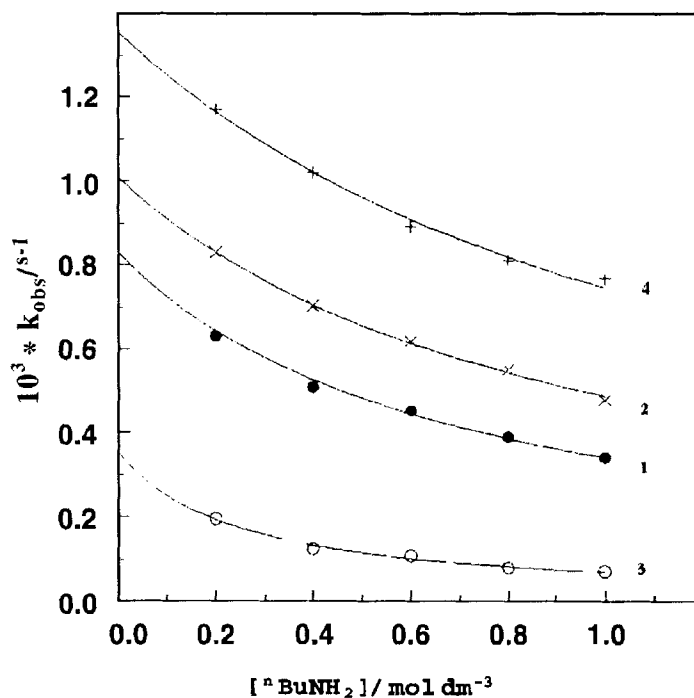
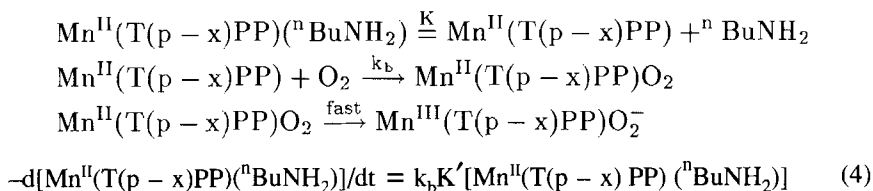


FIGURE 2 Dependence of k_{obs} on the concentration of $^n\text{BuNH}_2$. 1: $\text{Mn}^{\text{II}}(\text{TPP})(^n\text{BuNH}_2)$; 2: $\text{Mn}^{\text{II}}(\text{T}(p\text{-CH}_3)\text{PP})(^n\text{BuNH}_2)$; 3: $\text{Mn}^{\text{II}}(\text{T}(p\text{-Cl})\text{PP})(^n\text{BuNH}_2)$; 4: $\text{Mn}^{\text{II}}(\text{T}(p\text{-OCH}_3)\text{PP})(^n\text{BuNH}_2)$. The solid curves were calculated using equation (5).



The general rate law is given in (4), where $K' = K[\text{O}_2]/([^n\text{BuNH}_2] + K)$ is also approximately constant because dioxygen (its concentration¹² in chloroform saturation solution is about 10^{-3} mol dm^{-3} and $^n\text{BuNH}_2$ are in large excess. The *pseudo*-first-order rate constant is given in (5).

$$k_{\text{obs}} = k_b K' = k_b K' [\text{O}_2] / (^n\text{BuNH}_2 + K) \quad (5)$$

We obtained the equilibrium constant, K and the oxidation rate constant k_b from a nonlinear least-squares analysis of measured k_{obs} values with varying amounts of $^n\text{BuNH}_2$ (Table III). The small deviation between experiment and calculated data based on (5), lends support to the mechanism.

TABLE III Values for K and k_b for the reactions at 293K

	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -H	<i>p</i> -Cl
K	1.220	0.930	0.691	0.240
k_b	1.355	1.009	0.830	0.354
S	1.24×10^{-3}	6.34×10^{-4}	1.75×10^{-3}	9.60×10^{-4}

The mechanism indicates absorbance at time t (A_t), for instance at 440nm, is related to the absorbance of species $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})(^n\text{BuNH}_2)$ and $\text{Mn}^{\text{II}}(\text{T}(p-x)\text{PP})$. Together with the spectrophotometric method, we obtain

$$-\frac{dA_t}{dt} k_b A_t K [\text{O}_2] / ([^n\text{BuNH}_2] + K) = k_b K' A_t \quad (6)$$

that is, $\text{Ln}A_t = -k_b K' t = -k_{\text{obs}} t$. This also confirms that the oxidation mechanism we propose is reasonable.

Substituent Effects

The effect of substitution of the phenyl rings of tetraphenylporphinato complexes on the electronic properties and reactivities of the metal centre in our study can be adequately described by the Hammett relationships^{10, 13} given below.

$$\Delta \log k_{\text{obs}} = \log (k_{\text{obs}}^x / k_{\text{obs}}^H) = 4 \sigma \rho \quad (7)$$

$$\Delta E_{1/2} = E_{1/2}^x - E_{1/2}^H = 4 \sigma \rho_{EMF} \quad (8)$$

Here, σ is characteristic of electron donating/withdrawing properties of substituent x (the σ value for H is defined as 0.00) and ρ indicates the sensitivity of the reaction under study to substituent. In the case of a reversible electrochemical reaction, the Hammett ρ_{EMF} is related to the thermodynamic scale ρ_{ox} through the Nernst equation; then $\rho_{EMF} = -2.303(RT/nF) \rho_{ox} = -0.058 \rho_{ox}$ at 293K for a one-electron oxidation process.

In dealing with the *para*-substituted tetraphenylporphinat manganese (II) complexes, the equilibrium constants (K), the oxidation rate constants (k_b) and the half-wave potentials ($E_{1/2}$) for metal redox reactions agree reasonably well with the expected Hammett equation. Plots of $\log K$, $\log k_b$ and $E_{1/2}$ vs 4σ are shown in Figure 3. The calculated ρ_a , ρ_b and ρ_{EMF} are -0.345 , -0.280 and 0.0317 , respectively.

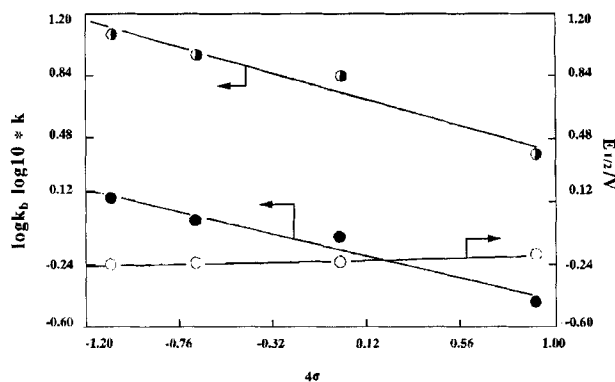


FIGURE 3 Hammett plots of $\log K$ vs 4σ (••••) $\log k_b$ vs. 4σ (••••) and $E_{1/2}$ (V) vs 4σ (•••). Values of 4σ used in this study are given in Table II.

The negative ρ_a and ρ_b values indicate that electron-donating groups favour the dissociation and oxidation processes, which can be interpreted as being due to stabilization of the positive charge on manganese by the electron-donating groups. The thermodynamic scale value ρ_{ox} for the one-electron oxidation process of (3) is -0.640 . This shows that electron-donating substituents also favour the electrochemical oxidation process and is consistent with the expected result that the rate constant for oxidation of manganese (II) porphyrin increases with increasing ease of oxidation (Mn^{II}/Mn^{III}) of the manganese centre. The ρ_{ox} value is larger than ρ_b , indicating that the removal of an electron from the manganese (II) porphyrin is more sensitive to electronic effects of substituents than to dioxygen coordination.

Acknowledgments

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