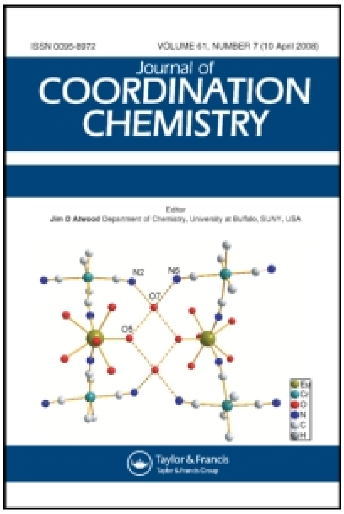

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KINETIC STUDIES OF THE REDUCTION OF CHLOROMANGANESE PORPHYRIN

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The reduction of manganese(III) porphyrins by hydrazine (L) was investigated by stopped-flow techniques. The mechanism of the reaction has been proposed based on the experimental results; the relationship between *pseudo*-first-order rate constants with the concentration of L. Calculated activation parameters showed that the pre-equilibrium step was exothermic and the reduction step endothermic. Substituent effects in the phenyl rings on the two steps have been examined.

Keywords: Manganese porphyrin; reduction; kinetics

INTRODUCTION

Manganese porphyrins continue to be of interest as catalysts for the epoxidation of olefins,[1] models for the behaviour of cytochrome P-450,[2] and DNA binding and cleavage reagent.[3] Axial ligation coupled with redox chemistry is important in many of these applications.[4,5] In the present report, the mechanism of the ligation and reduction of manganese(III) porphyrins by hydrazine (NH_2NH_2) as investigated. The reaction was studied in dimethylformamide (DMF) solution with a stopped-flow spectrophotometer. At high concentrations of $NH_2NH_2 \cdot H_2O$ (equal to or above a 1000-fold excess over $Mn^{III}(T(p\text{-x})PP)Cl$), the reduction followed first-order kinetics. Effects of tetra-*para*-substituents in TPP complexes on the reduction rate constants of $Mn^{III}(T(p\text{-x})PP)Cl)$ were also investigated.

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EXPERIMENTAL

Materials

$Mn^{III}(T(p\text{-}x)PP)Cl)$ (x = Cl, H, CH_3, OCH_3) complexes were synthesized and purified according to literature procedures.[6,7] Reagent grade DMF was treated with H type ion exchange resin and then distilled in vacuum under a stream of nitrogen. Hydrazine hydrate was used as received.

Measurements

The temperature of reaction solutions was controlled within ±0.1°C. Uncertainty of pressure was *ca* 0.5 MPa. Kinetic measurements were performed with a Type RA 401 stopped-flow instrument (Union Giken, Hirakata, Japan). The concentrations of the hydrazine were kept at a large excess over those of manganese(III) porphyrins to guarantee the *pseudo*-first-order conditions. The concentration of $Mn^{III}(T(p\text{-}x)PP)Cl)$ was approximately $5.0 \times 10^{-6}\,mol\,dm^{-3}$. Apparent first-order rate constants were obtained over at least 3 half-lives and represent the average of five to eight runs. Reproducibilities of the values of k_{obs} were better than ±5%. The change of axial ligation of Mn(II) and Mn(III) porphyrins as identified by conventional electronic absorption spectroscopy, infrared spectra and conductometric studies.

RESULTS AND DISCUSSION

The conductometric studies showed that $Mn^{III}(T(p\text{-}x)PP)Cl$ complexes are 1 : 1 electrolytes in DMF solution, consistent with the results of Schultz[7] that $Mn^{III}(TPP)Cl$ is converted into a *bis*(solvated) $Mn^{III}(TPP)(S)_2$ species in coordinating solvents such as DMF and DMSO. Following reduction, electronic absorption spectra exhibit a Soret band maximum at 438 nm and Q_a and Q_b band maxima at 572 and 612 nm. This reveals that the reduction product is the divalent manganese porphyrin.[8] In accordance with the terminology of Boucher,[9] these bands were numbered V, IV and III, respectively. The molar absorptivity ratios of bands III and IV ($\varepsilon_{III}/\varepsilon_{IV}$) and of band V $\varepsilon_V^{Mn(II)}/\varepsilon_V^{Mn(III)}$ are usually used to infer the identity of the axial ligation of Mn(II). Based on the results of Schultz,[7] it is reasonable to deduce that in the reduction process the potential ligand L (NH_2NH_2) would replace the solvent DMF at the axial sites. The values of $\varepsilon_{III}/\varepsilon_{IV}$ and $\varepsilon_V^{Mn(II)}/\varepsilon_V^{Mn(III)}$ were 1.00

and 2.10 in our experiments, while when DMF is the axial ligand, the values were 0.89 and 4.04, respectively. In our infrared experiments, the existence of ν_{N-H} bands at 3336 and 3262 cm^{-1} also gave good support for NH_2NH_2 as the axial ligand in the divalent manganese porphyrin.

The reduction of manganese porphyrins by L in DMF has been studied by stopped-flow spectrophotometry. Reactions were initiated by mixing solution which we shall refer to as solution A and solution B throughout the text. Solution A contained $Mn^{III}(T(p\text{-}x)PP)Cl$ while solution B contained L. The concentrations of reagents employed in the experiments are provided either in the Tables or in the Figure legends.

Since there is a large difference (*ca* 30 nm) between the position of the Soret band of $Mn^{III}(T(p\text{-}x)PP)Cl$ ($\lambda = 465$ nm) and $Mn^{II}(T(p\text{-}x)PP)(L)$ ($\lambda = 438$ nm), we can follow the reduction of the manganese(III) porphyrin by spectrophotometrically monitoring the disappearance of absorbance at 465 nm ($\varepsilon = 70000-104000\ M^{-1}\ cm^{-1}$, DMF). At this wavelength, the absorbances of the divalent manganese porphyrin species are minimal.

Mixing solution A and solution B resulted in a decrease in A_{465} which followed the first-order rate law. The reduction of $Mn^{III}(T(p\text{-}x)PP)Cl$ to $Mn^{II}(T(p\text{-}x)PP)(L)$ was a *pseudo*-first-order reaction under our experimental conditions. A typical relationship between the *pseudo*-first-order rate constants with the concentration of L is shown in Figure 1.

Mechanism

Figure 1 obviously shows that an increase in the concentration of L causes an increase of the k_{obs} value, the whole process was not first order with respect to L. Plots of $1/k_{obs}$ of the reduction of $Mn^{III}(T(p\text{-}x)PP)Cl$ by L *vs* 1/[L] at various temperatures all gave straight lines with good correlation coefficients ($r > 0.999$). Based on the above analysis, we propose the reduction mechanism below, where $Por = (T(p\text{-}x)PP)^{2-}$.

$$Mn^{III}(Por)Cl \xrightarrow{DMF} Mn^{III}(Por)^{+}Cl^{-} \tag{1}$$

$$Mn^{III}(Por)^{+}Cl^{-} + L \overset{K}{\rightleftharpoons} Mn^{III}(Por)(L)^{+}Cl^{-} \tag{2}$$

$$Mn^{III}(Por)(L)^{+}Cl^{-} \xrightarrow{k} Mn^{II}(Por) + \text{product} \tag{3}$$

$$Mn^{II}(Por) + L \xrightarrow{fast} Mn^{II}(Por)(L) \tag{4}$$

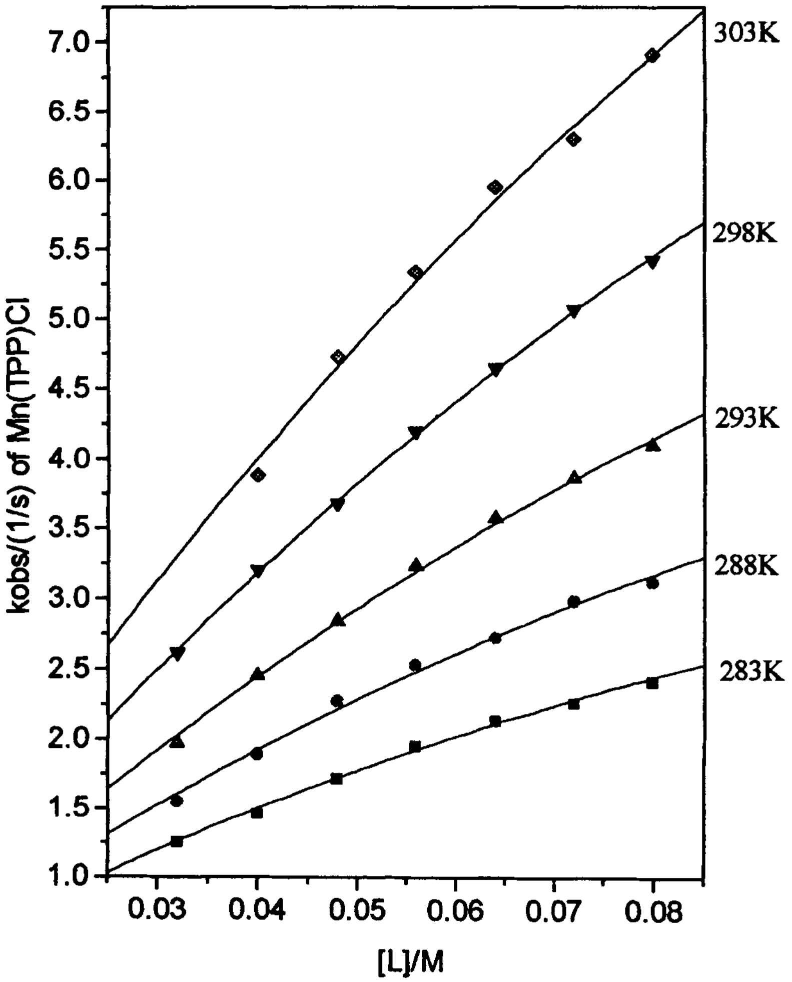

FIGURE 1 Dependence of the apparent first-order rate constant k_{obs} on the concentration of L at various temperatures; $[MnTPPCl] = 5.0 \times 10^{-6}\,mol\,dm^{-3}$.

By applying the steady-state approximation to the $Mn^{II}(Por)$ intermediate, we obtain the general rate law as follows.

$$-\frac{d[Mn^{III}(Por)^{+}Cl^{-}]}{dt} = \frac{kK[L]}{(1+K[L])}[Mn^{III}(Por)^{+}Cl^{-}] \qquad (5)$$

The *pseudo*-first-order rate constant is given by (6).

$$k_{obs} = \frac{kK[L]}{1+K[L]} \qquad (6)$$

Values of the pre-equilibrium constant, K, and the rate constant, k, were obtained by using a non-linear least-squares program based on the dependence of the k_{obs} data on the concentration of L. The small deviation between the experimental data and theory (the solid line as shown in Figure 1) gave good support for the proposed mechanism. This also shows that absorbance at time t (A_t) is related to the absorbance of $Mn^{III}(Por)^+Cl^-$, $Mn^{III}(Por)(L)^+Cl^-$ and $Mn^{II}(Por)(L)$. Together with the spectrophotometric method, we obtained

$$-\frac{dA_t}{dt} = \frac{kK[L]}{1+K[L]}(A_t - A_\infty) = k_{obs}(A_t - A_\infty) \qquad (7)$$

that is, $\ln(A_t - A_\infty)/(A_0 - A_\infty) = -k_{obs}t$. This also confirms that the reduction mechanism we propose is reasonable.

Temperature Effects

Temperature effects on the pre-equilibrium constant, K, and the rate constant, k, were different. Values of standard changes of molar enthalpy and entropy and activation enthalpy and entropy were estimated by fitting the variable temperature data of K and k to the Vant Hoff and Eyring equations, respectively. Results are listed in Table I.

Table I shows that the pre-equilibrium step is an exothermic reaction and the reduction step is an endothermic reaction. By comparing the obtained activation parameters, an isokinetic relationship between ΔH_m^o and ΔS_m^o was found (correlation coefficient $r > 0.9999$), while there was no such relationship between $\Delta H_m^{\neq}$ and $\Delta S_m^{\neq}$.

Substituent Effects

The effect of substitution in the phenyl rings of (tetraphenylporphinato)-managanese complexes on electronic properties and reactivities of the metal

TABLE I Activation parameters for the reduction reaction of the Mn(T(*p*-x)PP)Cl complexes with L

	p-OCH₃	*p-CH₃*	*p-H*	*p-Cl*
ΔH_m^o(kJ/mol)	−9.90 ± 0.06	−10.51 ± 0.07	−17.24 ± 0.10	−30.29 ± 0.19
ΔS_m^o(J/mol K)	−22.26 ± 0.24	−23.48 ± 0.25	−44.20 ± 0.33	−85.06 ± 0.66
$\Delta H_m^{\neq}$(kJ/mol)	48.97 ± 0.11	47.60 ± 0.09	46.63 ± 0.07	51.03 ± 0.17
$\Delta S_m^{\neq}$(J/mol K)	−58.52 ± 0.39	−62.51 ± 0.31	−64.51 ± 0.23	−42.78 ± 0.59

Errors give represent one standard deviation.

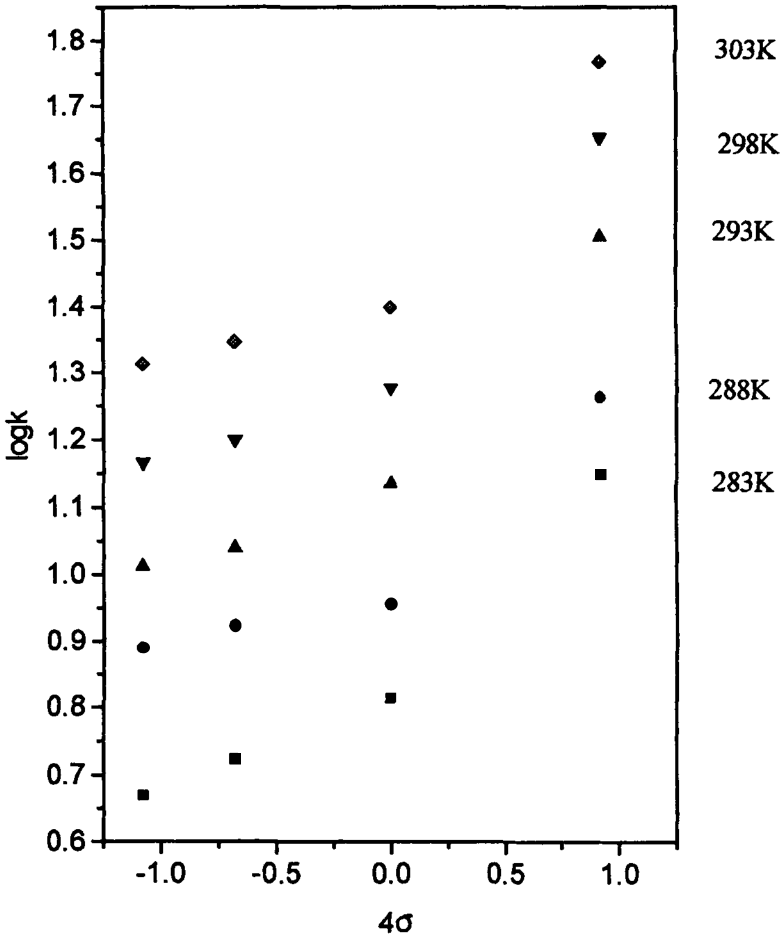

FIGURE 2 Plots of log k *vs* 4σ at different temperatures.

centre in our study can be adequately described by the Hammett relationship[8] in (8).

$$\Delta \log K = \log(K^X/K^H) = 4\sigma\rho \tag{8}$$

Here, σ is a characteristic of the 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 substituents. In dealing with the *para*-substituted (tetraphenylporphinato)manganese(III) complexes, the pre-equilibrium constants agree reasonably well with the expected Hammett equation at different temperatures. The correlation coefficient, r, of log K *vs* 4σ was larger than 0.99. The calculated ρ values were all positive and attenuate when the temperature is raised. Plots of log k *vs* 4σ are shown in Figure 2. These indicate that the effect of electron donating and withdrawing substituents on the reduction of trivalent manganese porphyrins is different, though reaction constants, ρ, are all positive.

Positive ρ values for the coordination of L to manganese(III) porphyrin and the reduction of the complexes at various temperatures are another indication that the electron-withdrawing groups favour the coordination and reduction processes, which can be interpreted as being due to the stabilization of negative charge on manganese by the electron-withdrawing groups, for both coordination and reduction involves the transfer of electron density from L to manganese.

Acknowledgments

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