Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Decreased Electron Transfer Rates of Manganese Porphyrins with Conformational Distortion of the Macrocycle[**]

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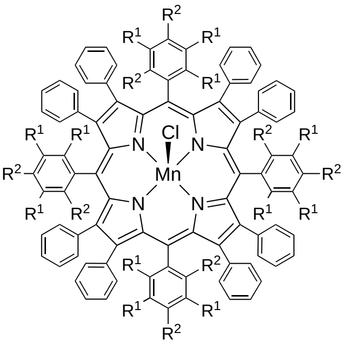
Nonplanar conformations of porphyrins have been suggested as being related to their functions in biological systems.[1–4] For example, a deformation of the porphyrin skeleton in heme and photosynthetic proteins is believed to arise from environmental effects.[3, 5, 6] Synthetic dodecaphenylporphyrins which contain a phenyl ring at each β-pyrrole and *meso* position of the porphyrin macrocycle are known to adopt a nonplanar conformation.[3, 7–9] Nonplanarity of the porphyrin ring due to steric repulsion between ring substituents in dodecasubstituted porphyrins affects their optical properties.[7–11] Manganese is an essential metal in several biological systems that are involved in electron transfer reactions,[12] and extensive efforts have therefore been devoted to elucidating electron transfer processes in synthetic manganese porphyrins.[13–16] However, there have been so far no reports on how conformational distortions of the porphyrin ring affect the rates of homogeneous electron transfer reactions in manganese or other transition metal porphyrins.

Here we report the homogeneous electron transfer kinetics for reduction of [(P)MnCl], where P represents the dianion of tetraphenylporphyrin (tpp) or of the dodecaphenylporphyrins (dpp-X, X = H_{20}, $Cl_{12}H_8$, F_{20}). The relationship between the logarithms of the rate constants of electron transfer and the free energy change of electron transfer gives an initial evaluation of reorganization energies λ for reduction of manganese porphyrins with a planar macrocycle, as in [(tpp)MnCl], and a nonplanar macrocycle, as in [(dpp-X)MnCl].



[(P)MnCl]
[(dpp-H_{20})MnCl]: $R^1 = R^2 = H$
[(dpp-$Cl_{12}H_8$)MnCl]: $R^1 = Cl$, $R^2 = H$
[(dpp-F_{20})MnCl]: $R^1 = R^2 = F$

Previous studies of the electrochemistry of [(dpp-X)MnCl] in benzonitrile show that the reduction of Mn^{III} to Mn^{II} is quasireversible[16] and that the potential separation between the cathodic and anodic peak potentials, $\Delta E_p = |E_{pc} - E_{pa}|$, increases in the order [(tpp)MnCl] < [(dpp-H_{20})MnCl] < [(dpp-$Cl_{12}H_8$)MnCl] < [(dpp-F_{20})MnCl] (Table 1).[17] The large ΔE_p value (0.52 V) for the reduction of [(dpp-F_{20})MnCl] may be related to the dissociation of Cl^- after reduction of Mn^{III} to Mn^{II}. However, the fact that the magnitude of ΔE_p remains unchanged after addition of an excess of Cl^- (0.1 M) suggests that the large ΔE_p value is due to slow electron transfer kinetics, as reported for other [(P)MnCl] complexes[15, 18] whose kinetics have been determined by electrochemical methods.[15, 18, 19]

The slow electron transfer in the reduction of [(dpp-X)MnCl] and [(tpp)MnCl] was confirmed in the present study by measuring the kinetics of the homogeneous electron transfer reduction with semiquinone radical anions as chemical reductants whose oxidation potentials[20] are low enough to reduce each Mn^{III} porphyrin to its Mn^{II} form. These reducing agents were prepared by comproportionation of the *p*-benzoquinone derivatives with the corresponding hydroquinone dianions, which were generated by reactions of hydroquinones with tetramethylammonium hydroxide.[21] The kinetics of electron transfer from the semiquinone radical anion to [(tpp)MnCl] or [(dpp-X)MnCl] were then followed by monitoring the increase in absorbance of the Mn^{II} Soret band (e.g., at 488 nm for [(dpp-H_{20})MnCl]).

The electron transfer rate obeys a second-order rate law when the initial concentrations of [(dpp-X)MnCl] and the semiquinone radical anion are equal. The observed second-

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Table 1. Rate constants k_{et} and free energy changes ΔG^0_{et} for electron transfer reduction of [(P)MnCl] with semiquinone radical anions $XQ^{\bullet-}$ in deaerated MeCN at 298 K, their one-electron redox potentials E^0_{red}[a] and E^0_{ox}[b] versus SCE, and reorganization energies λ_{22} for the self-exchange reaction of [(P)MnCl]/[(P)MnCl]$^-$.

[(P)MnCl]	E^0_{red} (ΔE_p)[c] [V]	$XQ^{\bullet-}$[d]	E^0_{ox} [V]	k_{et}[e] [$M^{-1}s^{-1}$]	ΔG^0_{et} [eV]	λ_{22}[f] [kcal mol^{-1}]
[(dpp-H_{20})MnCl] (**1**)	−0.36 (0.13)	2,6-$Me_2Q^{\bullet-}$	−0.67	4.7×10^5	−0.31	67
		$MeQ^{\bullet-}$	−0.58	4.1×10^4	−0.22	72
		$Q^{\bullet-}$	−0.50	1.3×10^4	−0.14	71
[(dpp-$Cl_{12}H_8$)MnCl] (**2**)	−0.15 (0.25)	2,6-$Me_2Q^{\bullet-}$	−0.67	2.8×10^5	−0.52	86
		$MeQ^{\bullet-}$	−0.58	1.2×10^5	−0.43	84
		$Q^{\bullet-}$	−0.50	8.6×10^4	−0.35	79
[(dpp-F_{20})MnCl] (**3**)	0.04 (0.52)	2,6-$Me_2Q^{\bullet-}$	−0.67	2.3×10^6	−0.71	89
		$MeQ^{\bullet-}$	−0.58	1.3×10^6	−0.62	86
		$Q^{\bullet-}$	−0.50	2.0×10^5	−0.54	89
		$ClQ^{\bullet-}$	−0.34	1.2×10^5	−0.38	79
[(tpp)MnCl] (**4**)	−0.22 (0.07)[g]	$Q^{\bullet-}$	−0.50	5.4×10^7	−0.28	41
		$ClQ^{\bullet-}$	−0.34	3.4×10^7	−0.12	31
		2,5-$Cl_2Q^{\bullet-}$	−0.18	6.1×10^5	0.04	38

[a] Determined in PhCN unless otherwise noted; 0.1 M TBAP, scan rate 0.1 V s^{-1};[14] the experimental error is within ±0.005 V. [b] Taken from ref. [18]; the experimental error is within ±0.005 V. [c] The values of peak potential separation expressed in volts are given in parentheses. [d] 2,6-Me_2Q = 2,6-dimethyl-*p*-benzoquinone, MeQ = methyl-*p*-benzoquinone, Q = *p*-benzoquinone, ClQ = chloro-*p*-benzoquinone, 2,5-Cl_2Q = 2,5-dichloro-*p*-benzoquinone. [e] The experimental error is within ±5%. [f] Obtained from Equation (1). [g] Determined in MeCN, 0.1 M TBAP, scan rate 0.1 V s^{-1}.[17]

order rate constants k_{et} of the electron transfer reactions are summarized in Table 1, which also lists redox potentials of the porphyrin and the reducing agent as well as the free energy change of electron transfer from the semiquinone radical anion to [(P)MnCl] (ΔG^0_{et}). It was confirmed that the k_{et} value for electron transfer from semiquinone radical anion ($Q^{\bullet-}$) to [(dpp-F_{20})MnCl] in the presence of 0.1 M tetrabutylammonium chloride ($1.8 \times 10^5 M^{-1} s^{-1}$) is essentially the same as the value in the absence of excess Cl^- ($2.0 \times 10^5 M^{-1} s^{-1}$). The ΔG^0_{et} values were calculated from the one-electron reduction potentials of [(P)MnCl] (E^0_{red}) and the one-electron oxidation potentials of the semiquinone radical anions (E^0_{ox}), which are equivalent to the one-electron reduction potentials of the corresponding quinones.[20]

Reorganization energies λ_{22} for the self-exchange reaction of [(P)MnCl]/[(P)MnCl]$^-$ are listed in Table 1 and were determined by using Equation (1), which is readily derived from the Marcus equation;[22] $\Delta G^{\neq}$ is the free energy of

$$\lambda_{22} = 2(2\Delta G^{\neq} - \Delta G^0_{et} + 2[\Delta G^{\neq}(\Delta G^{\neq} - \Delta G^0_{et})]^{1/2}) - \lambda_{11} \quad (1)$$

$$\Delta G^{\neq} = (2.3RT/F)\lg[Z(k_{et}^{-1} - k_{diff}^{-1})] \quad (2)$$

activation, and λ_{11} is the reorganization energy for the self-exchange reaction of $XQ/XQ^{\bullet-}$. A λ_{11} value of 16.9 kcal mol^{-1} for $Q/Q^{\bullet-}$ was determined from the linewidth variation of the EPR spectrum of semiquinone radical anion ($Q^{\bullet-}$) in the presence of various concentrations of *p*-benzoquinone (Q) in PhCN at 298 K.[23] The λ_{11} values of other semiquinone radical anion derivatives were assumed to be the same as that of $Q/Q^{\bullet-}$. The $\Delta G^{\neq}$ values were obtained from the observed rate constant of electron transfer k_{et} and the diffusion rate constant k_{diff} by Equation (2); Z is the collision frequency (taken as $1 \times 10^{11} M^{-1} s^{-1}$), F is the Faraday constant, and the k_{diff} value in MeCN is $2.0 \times 10^{10} M^{-1} s^{-1}$.

The reorganization energies depend significantly on the type of porphyrin macrocycle, and the λ_{22} values (mean values, in kcal mol^{-1}) increase in the order [(tpp)MnCl] (37 ± 4) < [(dpp-H_{20})MnCl] (70 ± 2) < [(dpp-$Cl_{12}H_8$)MnCl] (83 ± 3) ≈ [(dpp-F_{20})MnCl] (86 ± 4). Hence, the electron transfer rate at a given free energy change of electron transfer should decrease in this order. This is clearly shown in Figure 1, in which the $\lg k_{et}$ values are plotted against ΔG^0_{et} for electron transfer from $XQ^{\bullet-}$ to [(P)MnCl] in MeCN at 298 K. The fit of the curves to the Marcus theory of adiabatic outer-sphere electron transfer[22] for the reorganization energies of the cross-reactions between [(P)MnCl] and $XQ^{\bullet-}$ ($\lambda = (\lambda_{11} + \lambda_{22})/2$) indicates that the rate variations at a given ΔG^0_{et} value arise from the difference in the λ value and not from the non-adiabaticity.

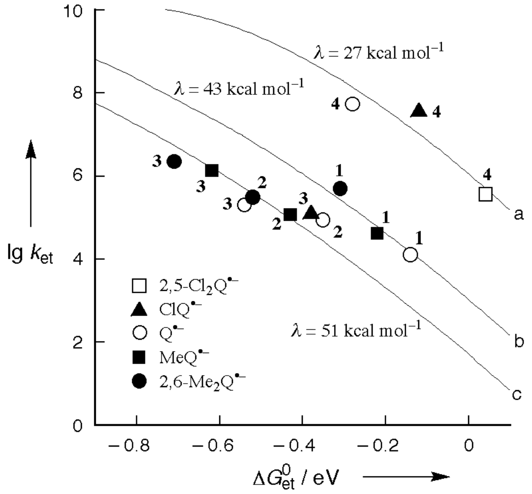

Figure 1. Dependence of $\lg k_{et}$ on ΔG^0_{et} for the electron transfer reductions of the [(P)MnCl] derivatives **1**–**4** by semiquinone radical anions in deaerated MeCN at 298 K. Curve a: P = tpp (**4**); curve b: P = dpp-H_{20} (**1**); curve c: P = dpp-$Cl_{12}H_8$ (**2**), P = dpp-F_{20} (**3**). For explanation of abbreviations, see Table 1. The λ values are calculated by using the Marcus theory of adiabatic outer-sphere electron transfer.

The crystal structure of [(dpp-F_{20})MnCl] reveals a non-planar conformation of the macrocycle because of peripheral congestion of the porphyrin.[16] The Mn^{III} center is located inside the curved surface of the nonplanar porphyrin macrocycle. Such a distorted conformation results in appreciably shorter Mn^{III}–N distances (1.99(1) Å)[16] than in planar [(tpp)MnCl] (2.009 Å).[24] Such strong binding of Mn^{III} to the nonplanar porphyrin results in major bond reorganization on reduction of Mn^{III} to Mn^{II}, which is accompanied by out-of-plane displacement since an electron is added to the $d_{x^2-y^2}$ orbital, which directly interacts with the orbitals of the pyrrole nitrogen atoms.[24] Hence, the greater the nonplanarity of the porphyrin ligand, the stronger the binding of Mn^{III} to the ligand and the larger the reorganization energy of the electron transfer reduction, as was experimentally observed in the present study. The fact that the E^0_{red} value of [(dpp-H_{20})MnCl] (−0.36 V) is more negative than that of [(tpp)MnCl] (−0.22 V), in spite of the electron-withdrawing effect of the additional phenyl groups in dpp-H_{20} (Table 1), is also ascribed to the stronger Mn^{III}–N binding of the nonplanar conformation of the dpp-H_{20} ligand, as compared with the planar tpp ligand.

In conclusion, the rate of electron transfer reduction of a Mn^{III} to a Mn^{II} porphyrin is significantly slowed by conformational distortions of the porphyrin ring.

Experimental Section

Syntheses and characterization of the [(P)MnCl] complexes have been previously reported.[16] Redox potentials of [(P)MnCl] in PhCN or MeCN containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte were determined at room temperature by cyclic voltammetry under deaerated conditions with a three-electrode system and a BAS 100B electrochemical analyzer. Kinetic measurements for electron transfer from $XQ^{\bullet-}$ to [(P)MnCl] were carried out with a Union RA-103 stopped-flow spectrophotometer under deaerated conditions. The rates of electron transfer were followed by monitoring the increase in spectral absorbance of the reduced porphyrin under second-order conditions with equal initial concentrations of [(P)MnCl] and the $XQ^{\bullet-}$. Second-order rate constants were determined by least-squares curve fitting on a Macintosh microcomputer. The second-order plots of $(A_\infty - A)^{-1}$ versus time (A_∞ and A are the final absorbance and the absorbance at the reaction time, respectively) were linear for three or more half-lives (correlation coefficient $\rho > 0.999$).

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