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Communications

Correlation of Heterogeneous Electron-Transfer Rate with Electron-Transfer Site in Metalloporphyrins

The question of whether electron transfer takes place at metal or porphyrin sites is an important and often controversial issue in metalloporphyrin redox chemistry.[1-5] In addition to electronic absorption,[6] infrared,[7] NMR,[8] ESR,[9] and Raman[3a,10] spectroscopic techniques, electrochemical measurements have been used to make this assignment. Electrochemically, an electron transfer is assumed to be centered on the porphyrin ring if its half-wave potential (a) occurs at a constant potential difference from a known ring-centered reaction[11] or (b) is insensitive to changes in axial ligation.[2c] Although these criteria have been helpful in assigning the site of electron transfer, they are not infallible.[1a]

In this communication we report that observation of another electrochemical parameter, the standard heterogeneous rate constant ($k_{s,h}$),[12] and its temperature dependence can assist in assigning the site of electron transfer in metalloporphyrins. The determination is based on the realization from the Marcus theory[13] that $k_{s,h}$ will be small and will display a significant temperature dependence if the changes in nuclear coordinates that accompany electron transfer create a large activation barrier for the electrode reaction. Since larger changes in structure generally accompany metal- versus ring-centered redox processes in metalloporphyrins,[14] we expect that $k_{s,h}$ will correlate with the site of electron transfer in many cases. Also, as related factors influence the rate constants of homogeneous self-exchange reactions,[13a] the correlation should extend to electron-transfer reactions of metalloporphyrins in homogeneous solution. These hypotheses are supported by recent observations from our laboratory that (i) for a series of oxomolybdenum(VI)–catecholate complexes electrode reactions centered on the metal are slow whereas those involving the catecholate ligand are fast[15] and (ii) the extent to which metal-centered electrode reaction rates of five-coordinate, high-spin porphyrins are diminished relative to those of six-coordinate, low-spin species correlates with the amount of metal atom out-of-plane displacement and axial ligand bond extension that occurs during electron transfer.[16]

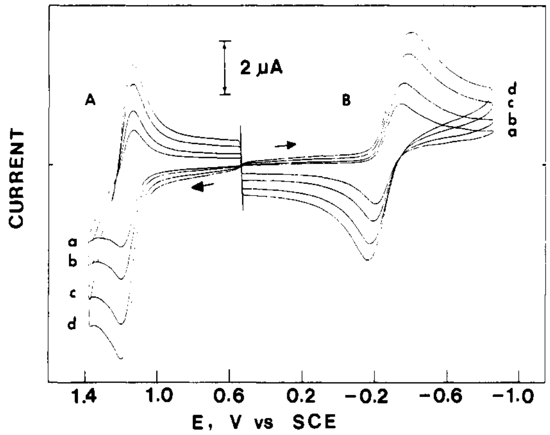

Figure 1. Cyclic voltammograms for oxidation (A) and reduction (B) of 0.45 mM Mn(TPP)Cl in 0.1 M BuN_4BF_4/CH_2Cl_2 at sweep rates of (a) 50, (b) 100, (c) 200, and (d) 300 mV s^{-1} at 298 K. Peak potential separations of 61, 62, 63, and 63 mV (A) and 150, 174, 212, and 240 mV (B) are observed at these sweep rates, respectively.

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Table I.[a] Half-Wave Potentials (V vs SCE), Peak Potential Separations (mV),[b] and Heterogeneous Electron-Transfer Rate Constants (cm s^{-1})[c] for Ring- and Metal-Centered Electrode Reactions of Metalloporphyrins

	ring centered					metal centered				
		298 K		221 K			298 K		221 K	
complex	$E_{1/2}$	ΔE_p	$10^3 k_{s,h}$	ΔE_p	$10^3 k_{s,h}$	$E_{1/2}$	ΔE_p	$10^3 k_{s,h}$	ΔE_p	$10^3 k_{s,h}$
$Mn^{III}(TPP)Cl$	1.21	62	>100	45	>100	−0.29	177	1.9	500	0.0072
$Zn^{II}(TPP)$	0.98	58	>100	44	>100					
	−1.29	57	>100	46	>100					
$Fe^{III}(TPP)Br$	1.16	62	>100	45	>100	−0.18[d]	82[d]	10[d]		
$Fe^{III}(TPP)Cl$	1.18	57	>100	44	>100	−0.32[d]	91[d]	6.9[d]		
$Fe^{III}(TPP)OCH_3$	*e*	*e*	*e*	43	>100	−0.79[d]	130[d]	1.1[d]		
$Co^{II}(TPP)$						−0.77	*e*	*e*	50	24
$Fe^{III}(TPP)(Im)_2^+$						−0.21	68	25	57	8.5

[a] Recorded for ca. 0.5 mM solutions of complexes in 0.1 M Bu_4NBF_4/CH_2Cl_2 at 0.02-cm^2 Pt[Mn(TPP)Cl, Fe(TPP)Cl, $Fe(TPP)(Im)_2^+$, Zn(TPP)] or Au[Fe(TPP)Br, $Fe(TPP)OCH_3$, Co(TPP)] electrodes. Ring-centered reactions are oxidations and metal-centered reactions are reductions except for Zn(TPP) for which a ring-centered oxidation and a ring-centered reduction are shown. [b] Value at 0.1 V s^{-1}; uncertainty ±2 mV. [c] Evaluated from variation in ΔE_p with sweep rate for $v = 0.05$–0.3 V s^{-1}; uncertainty ±20%. [d] From ref 16. [e] A chemical reaction following the electrode reaction at room temperature precludes obtaining kinetic data.

The relationship is best illustrated by the cyclic voltammograms[17] of Mn(TPP)Cl[21] in Figure 1. The positively swept voltammograms correspond to the porphyrin-centered oxidation

$$Mn^{III}(TPP)Cl \rightleftharpoons Mn^{III}(TPP^{\bullet})Cl^+ + e^- \quad (1)$$

whereas the negatively swept voltammograms represent the metal-centered reduction[22]

$$Mn^{III}(TPP)Cl + e^- \rightleftharpoons Mn^{II}(TPP)Cl^- \quad (2)$$

Reaction 1 is electrochemically reversible. Its peak potential separation (ΔE_p) is independent of sweep rate and equal to a value (62 ± 2 mV) consistent with Nernstian one-electron transfer accompanied by a small amount of edge diffusion.[24] Similar behavior is exhibited by other reactions that are known to be porphyrin-centered. For example, Table I shows that the one-electron oxidation and reduction of Zn(TPP), which contains a redox-inactive metal center, exhibit sweep-rate independent, Nernstian values of ΔE_p at 298 and 221 K. Since the charge added to or removed from the ring in the course of these reactions is delocalized over a 24-atom framework, metalloporphyrins exhibit little change in structure upon reduction or oxidation to their π radical anions and cations.[25] A small structural change results in a small inner-shell reorganization energy, which, together with a modest outer-shell reorganization energy anticipated[13b] on the basis of large porphyrin size, presents a relatively small total activation barrier to the electrode reaction. Consistent with this expectation we find that increasing the sweep rate to values above those shown in Figure 1 ultimately leads to increases in ΔE_p that are the result of uncompensated solution resistance and cause us to assign a lower limit of $k_{s,h} \geq 0.1$ cm s^{-1} to the porphyrin-centered reactions.

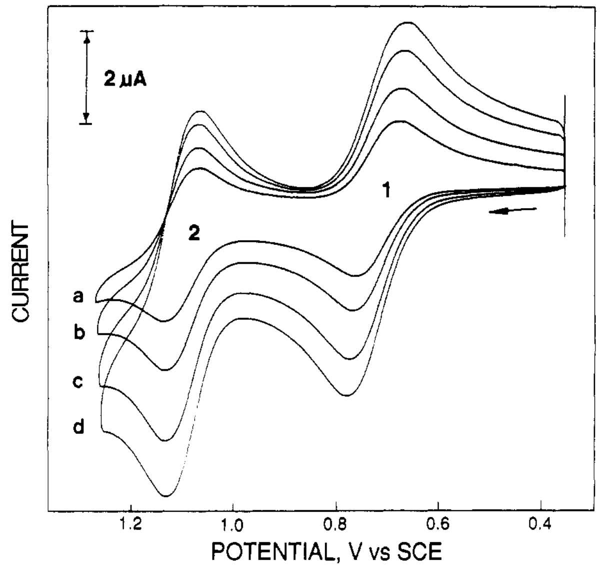

Figure 2. Cyclic voltammograms for oxidation of 0.41 mM Co(TPP) in 0.1 M Bu_4NBF_4/CH_2Cl_2 containing 0.035 M CH_3OH at sweep rates of (a) 50, (b) 100, (c) 200, and (d) 300 mV s^{-1} at 298 K. Peak potential separations of 78, 90, 105, and 117 mV (first wave) and 58, 58, 59, and 60 mV (second wave) are observed at these sweep rates, respectively.

Reaction 2 is electrochemically quasireversible. A value of $k_{s,h} = (1.9 \pm 0.3) \times 10^{-3}$ cm s^{-1} is determined from the variation in its peak potential separation with sweep rate at 298 K. The small

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(17) Electrode kinetic measurements were carried out by cyclic voltammetry[18] in 0.1 M Bu_4NBF_4/CH_2Cl_2 at 0.02-cm^2 Pt or Au electrodes (Bioanalytical Systems, West Lafayette, IN) using the electrochemical cell and instrumentation described in ref 19. The cell design minimizes uncompensated solution resistance by a combination of close placement of working and reference electrodes and instrumental positive feedback. For the electrode spacing, solvent/supporting electrolyte conditions and resistance compensation settings used in this work we estimate that 20 and 35 Ω of residual uncompensated solution resistance exists between the working and reference electrodes at 298 and 221 K, respectively. For 0.5 mM solutions of electroactive material these resistances contribute ≤1 mV of uncompensated *iR* drop to the voltammetric peak potential separations at sweep rates ≤0.3 V s^{-1}. Absence of uncompensated resistance effects was verified by examining the reversible oxidation of ferrocene ($k_{s,h} \geq 1$ cm s^{-1})[20] under identical experimental condition.

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(21) Abbreviations: TPP = tetraphenylporphyrin dianion, Im = imidazole, TMP = tetramesitylporphyrin dianion.

(22) Evidence that chloride ion remains bound to Mn(II) after reduction of the metal center is provided by visible wavelength spectroelectrochemistry. The product of reaction 2 exhibits a Soret band at 444 nm and three additional adsorption maxima at 532, 574, and 618 nm. These spectral features are identical with those of five-coordinate $Mn^{II}(TMP)X^-$ derivatives and distinct from those of four-coordinate $Mn^{II}(TMP)$,[21,23] indicating that the product of reaction 2 is five-coordinate.

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(25) X-ray crystallographic studies of porphyrin π cation radicals[2d,f,14b] indicate that bond distances and bond angles within the porphyrin core and the geometric aspects of metal coordination are unchanged by removal of an electron from neutral porphyrin.[26] Thus, as is the case for organic electrode reactions involving little structural change,[27] heterogeneous charge-transfer reactions of porphyrin rings should be rapid.

(26) Four- and five-coordinate metalloporphyrin π cation radicals exhibit a ruffled porphyrin core, but as the ring is easily deformed in the direction perpendicular to its plane,[14b] this distortion is not expected to make a significant contribution to the overall activation energy barrier.

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electron-transfer rate constant is the result of a large difference in structure between the reactant and product of reaction 2. X-ray crystal structures show that the Mn atom residues 0.27 Å above the porphyrin plane in $Mn^{III}(TPP)Cl$[28] versus 0.64 Å in $Mn^{II}(TPP)Cl^-$,[29,22] apparently as a result of unfavorable interaction between the singly occupied metal $d_{x^2-y^2}$ orbital and the pyrrole nitrogens of the porphyrin ring. The significant inner-shell reorganization energy associated with this structural change is expected to result also in a large temperature dependence for the rate of the metal-centered electrode reaction. Table I shows that $k_{s,h}$ for reaction 2 decreases to 7.2×10^{-6} cm s^{-1} at 221 K, whereas reaction 1 retains essentially Nernstian behavior under these conditions.

Similar conclusions are reached regarding electrooxidation and -reduction of the iron(III) porphyrins Fe(TPP)X ($X^- = Br^-, Cl^-, CH_3O^-$). The metal-centered one-electron transfers of these species are quasireversible[16] (Table I) as a consequence of structural changes that include displacement of the Fe atom by an additional ~0.2 Å above the porphyrin plane and extension of the metal–axial ligand bond by ~0.1 Å upon Fe^{III} to Fe^{II} reduction. Although it has not been established that the axial ligand remains bound to the metal after reduction to Fe^{II}, the trend in the measured rate constants ($Br^- > Cl^- > CH_3O^-$) is thought to arise from the fact that the energy required to stretch the metal–axial ligand bond increases with increasing electron donor strength of the axial ligand. The one-electron porphyrin-centered oxidations of Fe(TPP)X exhibit Nernstian behavior within the limits of experimental uncertainty at 298 and 221 K. Correlation of a rapid electrode reaction rate with ring-centered electron transfer is significant particularly in the case of Fe(TPP)Cl oxidation, because the product of this reaction, which was once thought to be an iron(IV) species,[2b] is now definitely characterized as a porphyrin π cation radical.[2d,f] If the electron removed upon Fe(TPP)Cl oxidation had originated from a metal-centered orbital, the structural changes predicted[2d] upon Fe^{III} to Fe^{IV} oxidation would produce a detectably slow electrode reaction.

Another circumstance in which electron transfer at the metal can be distinguished from that at the ring is when the metal undergoes a change in coordination number during an electrode reaction. This behavior is illustrated by electrooxidation of four-coordinate $Co^{II}(TPP)$. Under rigorously noncoordinating conditions Co(TPP) is oxidized to its π cation radical,[4a] whereas in the presence of an intentionally added ligand such as methanol oxidation at the metal precedes that at the ring.[3,30]

$$Co^{II}(TPP) + 2CH_3OH \rightleftharpoons Co^{III}(TPP)(CH_3OH)_2^+ + e^- \qquad (3)$$

Figure 2 shows that the metal-centered character of the initial oxidation in the presence of methanol is detectable from its apparent electrode kinetics. The metal-centered oxidation at 0.72 V (eq 3) exhibits sweep-rate-dependent peak potential separations, whereas the porphyrin-centered oxidation at 1.10 V (eq 4) is

$$Co^{III}(TPP)(CH_3OH)_2^+ \rightleftharpoons Co^{III}(TPP^{\bullet})(CH_3OH)_2^{2+} + e^- \qquad (4)$$

electrochemically reversible. The apparent sluggishness of eq 3 presumably reflects the kinetics of association and dissociation of CH_3OH at the metal center rather than slow electron transfer resulting from a large inner-shell reorganization energy.

In the foregoing examples discrimination between metal- and ring-centered electron transfer on the basis of electrode kinetic behavior is made easily because the structural changes associated with the metal-centered reactions are large. However, in the event of other metal atom coordination geometries and/or spin states smaller changes in structure induced by the change in oxidation state may render the correlation between electron-transfer rate and electron-transfer site less definitive. To test this possibility, we examined the electrode reduction kinetics of four-coordinate $Co^{II}(TPP)$ and the low-spin, six-coordinate complex $Fe^{III}(TPP)(Im)_2^+$.[21]

$$Co^{II}(TPP) + e^- \rightleftharpoons Co^{I}(TPP)^- \qquad (5)$$

$$Fe^{III}(TPP)(Im)_2^+ + e^- \rightleftharpoons Fe^{II}(TPP)(Im)_2 \qquad (6)$$

In these geometries the metal atom remains essentially in the porphyrin plane and experiences little change in metal–porphyrin and metal–axial ligand distances upon reduction. However, Table I shows that the kinetics of reactions 5 and 6, although more facile than the metal-centered reductions of five-coordinate porphyrins, are less rapid than the essentially reversible porphyrin-centered oxidations. We surmise that either (i) the relatively small structural changes[31] that occur upon reduction of $Co^{II}(TPP)$ and $Fe^{III}(TPP)(Im)_2^+$ still constitute a significant inner-shell barrier to the electrode reaction or (ii) the more highly localized charge resulting from electron transfer at the metal center results in a larger outer-shell barrier.

In summary, the site of electron transfer in metalloporphyrins can be correlated with the heterogeneous rate constant of its electrode reaction in the event that large changes in structure accompany reduction or oxidation of the metal. In these cases, electron transfer at the metal is characterized by rate constants of $k_{s,h} \leq 0.01$ cm s^{-1}, whereas electron transfer at the ring is characterized by apparently reversible electrode kinetics ($k_{s,h} \geq 0.1$ cm s^{-1}). When minimal change in structure accompany electron transfer at the metal, rate constants of intermediate value are observed ($k_{s,h} = 0.01–0.1$ cm s^{-1}) and caution is advised in inferring the site of electron transfer from kinetic measurements in these cases.

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[30] The site of electron transfer in the absence and presence of CH_3OH was confirmed by visible wavelength spectroelectrochemistry. A broad, low-intensity Soret band is observed following one-electron oxidation of $Co^{II}(TPP)$ in carefully purified CH_2Cl_2 whereas a red-shifted Soret band of high intensity is observed in the same experiment in the presence of methanol.

[31] On the basis of X-ray crystallographic information, these changes are estimated to be 0.007 Å in the Co–N_p distance for Co(TPP) reduction[32] and 0.04 Å in the Fe–N_{Im} distance and ≤0.01 Å in the Fe–N_p distance for $Fe(TPP)(Im)_2^+$ reduction.[14,33]

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Department of Chemistry
Purdue University School of Science
Indiana University-Purdue University at Indianapolis
Indianapolis, Indiana 46205

Xi Hai Mu
Franklin A. Schultz*

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Preparation and Characterization of a Layered Molybdenum Phosphate with Mo–Mo Bonds: Structure of $Na_3Mo_2P_2O_{11}(OH)\cdot 2H_2O$

There are a number of layered phosphate structures known for the p-, f-, and d-block elements, such as tin, uranium, titanium, zirconium, and vanadium, many of which are noted for their ion exchange or interlayer ionic mobility.[1] We have recently found a large number of new phosphate structure types, containing mixed octahedral–tetrahedral frameworks, in the molybdenum phosphate system using high-temperature solid-state reactions. Compounds such as $Cs_4Mo_8P_{12}O_{52}$,[2] $Cs_4Mo_{10}P_{18}O_{66}$,[3] and $Cs_3Mo_4P_3O_{16}$[4] were

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