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Nitrogen/Chlorine Atom Exchange Reactions between Manganese Porphyrins: Apparent Bridging Ligand Preference in an Inner-Sphere Process

In general, multielectron redox reactions are rare. Nonetheless, important examples of these processes are efficiently catalyzed by metalloenzymes such as xanthine oxidase, sulfite oxidase, nitrate reductase, and cytochrome P450. These enzymes apparently operate via an atom transfer process—the net result involves oxygen atom transfer in an overall two-electron redox reaction.[1] For most of these enzymes, there is little or no information on reaction pathways. Furthermore, it is difficult to model these enzymes because of the paucity of clearly established multielectron atom transfer processes. Development of systems that would allow studies of the rates, mechanisms, and energetics of multielectron reactions would clearly benefit our understanding of these important processes. Recently, a net three-electron transfer mediated by an unprecedented reversible nitrogen atom transfer was discovered in our laboratory.[2] As part of our continuing study of multielectron transfer, we now report that an analogous two-electron redox process can be mediated by reversible nitrogen atom transfer.

Using methods similar to those reported earlier,[2] we have found that reaction of (OEP)Mn≡N[3,4] with (TTP)Mn—Cl[3,5] in toluene results in a double exchange of axial ligands and a net two-electron transfer as illustrated in eq 1. The UV–vis spectra of this reaction,

$$\mathrm{(OEP)Mn^{V}{\equiv}N + (TTP)Mn^{III}{-}Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (OEP)Mn^{III}{-}Cl + (TTP)Mn^{V}{\equiv}N} \quad (1)$$

over several hours, show a gradual decrease in the intensity of Soret bands at 404 and 478 nm, indicating the disappearance of the starting nitrido and chloro complexes, respectively. New Soret bands simultaneously grow in at 422 and 360 nm, corresponding to the formation of (TTP)Mn≡N and (OEP)Mn—Cl, respectively. Since the nitrido complexes are diamagnetic, it is also possible to monitor this reaction by ^{1}H NMR. Thus, when (TTP)Mn—Cl and (OEP)Mn≡N are dissolved in $CDCl_3$, the loss of (OEP)Mn≡N can be followed by the decrease in intensity of NMR signals at δ 10.29 (s, 4 H, *meso*-H), 3.97 (m, 16 H, CH_2), and 1.85 (t, 24 H, CH_3). New peaks at δ 8.94 (s, 8 H, β-H), 8.04 (br, 8 H, *m*-H), 7.53 (d, 8 H, *o*-H) and 2.69 (12 H, CH_3) signify the formation of (TTP)Mn≡N. The reversibility of eq 1 was demonstrated in a similar manner by running the reaction in the opposite direction. The equilibrium for eq 1 favors the formation of (TTP)Mn≡N. This is in contrast to the analogous three-electron nitrogen atom transfer process, which slightly favors the formation of (OEP)Mn≡N. Equilibrium constants for eq 1 were measured by ^{1}H NMR in $CDCl_3$ at 22.0, 40.0, and 50.0 (±0.1) °C and are listed in Table I. From the temperature dependence of K_{eq} we find that $\Delta H = -6.94 \pm 0.14$ kcal/mol and $\Delta S = -17.2 \pm 0.5$ eu.

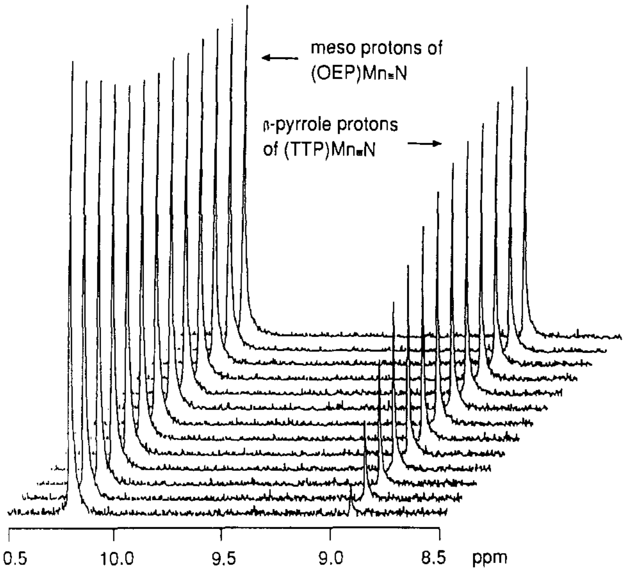

Figure 1. Stacked plot of kinetics run at 40.0 °C. $[(OEP)Mn{\equiv}N]_0 = 3.94 \times 10^{-3}$ M and $[(TPP)MnCl]_0 = 1.01 \times 10^{-3}$ M. Spectra were recorded at 20-min intervals.

Table I. Thermodynamic and Kinetic Parameters for Eq 1

T, K	K_{eq}	k_1, $M^{-1}\ s^{-1}$
295 ± 0.1	23.5 ± 3.6	0.010 ± 0.007
313 ± 0.1	12.1 ± 1.7	0.051 ± 0.005
323 ± 0.1	8.4 ± 2.1	0.150 ± 0.012

Rates for eq 1 were measured by ^{1}H NMR spectroscopy. A Bruker WM 300-MHz NMR spectrometer equipped with a variable-temperature probe was used for data accumulation and NMR1,[6] version 3.92, was used for data analysis. Known amounts of (OEP)Mn≡N and (TTP)Mn—Cl, in ratios varying from approximately 1:1 to 8:1 were transferred into NMR tubes, along with Ph_3CH as an internal standard. $CDCl_3$ was transferred into the NMR tubes under vacuum at −78 °C and the tubes were flame sealed under 670 Torr of N_2. Actual concentrations of starting reactants ranged from 6.25×10^{-4} to 9.18×10^{-3} M. Reaction progress was quantified by integration of the pyrrole β-proton signal of (TTP)Mn≡N (δ = 8.94) and the *meso*-proton signal of (OEP)Mn≡N (δ = 10.29). In all cases, the total amount of nitrido porphyrin complexes remained constant throughout the reaction as measured against Ph_3CH. Rate data were measured

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at 22.0, 40.0, and 50.0 (±0.1) °C. A typical kinetics run is shown in Figure 1.

The kinetic data were found to agree with an integrated rate law derived by King[7] for second-order reversible reactions. Similar rate constants, for a given temperature, were obtained from King's rate law regardless of the initial concentrations used. This indicates that the rate behavior of eq 1 is first order in each reactant. This is analogous to the second-order rate law found for the double ligand exchange between (OEP)Mn$\equiv$N and (TPP)Cr—Cl reported by Bottomley.[8] Rate constants for eq 1 are listed in Table I. The activation parameters for eq 1 derived from the rate data are $\Delta H^{\ddagger} = 17.4 \pm 1.4$ kcal/mol and $\Delta S^{\ddagger} = -8.7 \pm 1.0$ eu. These values are typical of those found for a variety of electron-transfer reactions.[9]

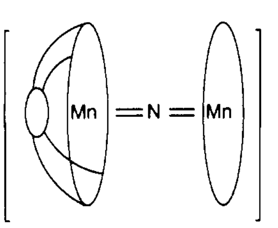
It is clear that eq 1 involves a formal two-electron redox process. Mechanistically, it is not likely that this reaction proceeds via an outer-sphere pathway. Evidence supporting this is provided by chemical reduction of nitrido manganese porphyrins. Buchler has shown that sodium anthracenide, an outer-sphere reagent, is capable of adding two electrons to the porphyrin ligand of (OEP)Mn$\equiv$N but does not reduce the metal.[10] Furthermore, Bottomley has demonstrated that the first and second electrochemical reductions of (OEP)Mn$\equiv$N and (TTP)Mn$\equiv$N are ligand-based.[11] Since eq 1 involves changes in the Mn oxidation states, it most likely proceeds through an inner-sphere mechanism.

Since chloro and nitrido ligands are both good bridging species, it is of fundamental interest to establish which is the preferred bridging ligand in this inner-sphere process. A series of mechanistic studies are all consistent with a pathway that involves initial chloride dissociation followed by nitrogen atom transfer through a μ-nitrido binuclear intermediate. For example, addition of 1 equiv of tetra-*n*-butylammonium chloride inhibits the rate by more than a factor of 1400. It is not likely that the excess chloride inhibits this reaction by taking up the sixth coordination site on the Mn(III) complex. In nonpolar solvents, only five-coordinate manganese(III) complexes have been observed.[12] Furthermore, replacement of the Mn(III) axial ligand with the more easily dissociated iodide ligand enhances the rate 500-fold, whereas use of the less easily dissociated acetate as the axial ligand decreases the reaction rate by a factor of 23 with respect to the chloride case.

Other evidence that supports the proposed mechanism is established by replacing the TTP ligand with Baldwin's C_2-capped porphyrin,[13] CAP, which has an aryl ring blocking one face of the macrocycle. Thus, when (CAP)Mn—Cl is treated with (OEP)Mn$\equiv$N, formation of (CAP)Mn$\equiv$N and (OEP)Mn—Cl is observed by ^{1}H NMR and UV-vis spectroscopy. In order for this reaction to proceed, it is likely that chloride must dissociate from the CAP complex before a μ-nitrido intermediate can form. Moreover, the reverse reaction, (CAP)Mn$\equiv$N plus (OEP)Mn—Cl, also proceeds to produce (CAP)Mn—Cl and (OEP)Mn$\equiv$N. Since the capped porphyrin prevents formation of a chloride bridge trans to the axial ligand of the starting nitride complex, this reaction most likely proceeds through a μ-nitrido-bridged intermediate. The most compelling argument for the existence of a μ-nitrido-bridged intermediate is evidenced by the reversibility of eq 2. The equilibrium constant for this process

$$\mathrm{(CAP)Mn{-}Cl + (OEP)Mn{\equiv}N \rightleftarrows (CAP)Mn{\equiv}N + (OEP)Mn{-}Cl} \quad (2)$$

is 4.8 ± 1.8 at 50 °C. Of the three possible intermediates, species I is the most chemically feasible for both the forward and reverse pathways for eq 2. Intermediate II is ruled out by the forward process while III is inconsistent with the reverse direction. Thus,



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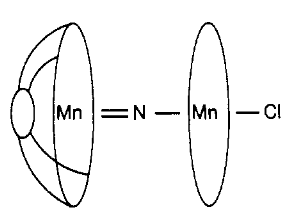

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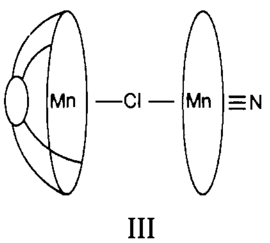

III

it appears that for nitrido/chloro ligand-exchange reactions of metalloporphyrins, a distinct preference for a bridging nitrido ligand over a bridging chloro ligand exists. This is consistent with a mechanism proposed by Bottomley[8] for an analogous process involving the reduction of (OEP)Mn$\equiv$N by (TPP)Cr—Cl. However, in this case, chloride dissociation from the chromium(II) complex is proposed not to precede formation of the μ-nitrido intermediate. Further work to elucidate the mechanisms of these atom-transfer processes is in progress.

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Oxo-Transfer Reactions of Chromium and Titanium Porphyrins

Examples of intermetal oxygen atom transfer are rare. In general, inner-sphere electron transfer mediated through an oxo ligand typically leads to formation of μ-oxo-bridged products.[1] For example, when $\mathrm{(TPP)Cr^{IV}{=}O}$ is treated with $\mathrm{Cr^{II}(TPP)}$ in toluene, formation of $\mathrm{(TPP)Cr^{III}{-}O{-}Cr^{III}(TPP)}$ is observed.[2,3] Intermetal oxo transfer thus far has been limited to molybdenum and tungsten complexes.[4] Oxo transfer between two ruthenium centers has been implicated in the aerobic epoxidation of olefins by ruthenium porphyrins.[5] As an extension of our studies on inner-sphere redox reactions and nitrogen atom transfer,[6] we have initiated an investigation of oxygen atom transfer. Our approach to oxo transfer developed as a result of our recent finding that nitrogen atom transfer occurs reversibly between (OEP)Mn$\equiv$N and (TTP)Mn—Cl as shown in eq 1.[7] Bottomley has shown that

$$\mathrm{(OEP)Mn{\equiv}N + (TTP)Mn{-}Cl \rightleftarrows (OEP)Mn{-}Cl + (TTP)Mn{\equiv}N} \quad (1)$$

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(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(2) Abbreviations: TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion.

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