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Reversible Nitrogen Atom Transfer between Nitridomanganese(V) and Manganese(III) Schiff-Base Complexes

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We are investigating the reactivity of nitridomanganese complexes of tetradentate Schiff-base ligands for the following reasons: (1) the Mn≡N moiety can undergo pseudodegenerate N$^-$-transfer reactions in porphyrin-based systems;[1−6] (2) certain synthetically useful organic reactions (e.g., olefin amination)[7] involve activated nitridomanganese complexes as reagents; (3) Mn≡N Schiff-base complexes are readily prepared and characterized; and (4) the remarkable steric and electronic tunability of salen-type ligands should facilitate systematic investigations of the reactivity of the Mn≡N center. In our work on the chemistry of (salen)Mn≡N **(1)** and (5,5′-(MeO)$_2$salchxn)Mn≡N **(2)**,[8] we have found the first example of reversible nitrogen atom transfer between metals in nonporphyrin complexes.[9]

Treatment of **1** with (5,5′-(MeO)$_2$salchxn)MnCl in dimethylformamide (DMF) in air results in spectral changes that establish the net two-electron (N$^-$) transfer described by eq 1.[10]

$$\begin{matrix}\text{(salen)Mn≡N } \mathbf{(1)} \\ + \\ \text{(5,5′-(MeO)}_2\text{salchxn)MnCl}\end{matrix} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \begin{matrix}\text{(salen)MnCl} \\ + \\ \text{(5,5′-(MeO)}_2\text{salchxn)Mn≡N } \mathbf{(2)}\end{matrix} \qquad (1)$$

As the reaction proceeds, there is a gradual decrease in intensities of near-UV absorption bands at 354 and 372 nm. These absorption changes correspond to the disappearance of the starting chloro and nitrido complexes, respectively. Two new near-UV bands at 398 and 408 nm simultaneously appear, indicating the formation of the products (salen)MnCl and **2**, respectively. The nitridomanganese(V) complexes were separated from their manganese(III) counterparts by column chromatography, and **2** was identified by ^{1}H NMR spectroscopy.[11]

To confirm the reversibility of the nitrogen atom transfer reaction, **2** was treated with (salen)MnCl. The final absorption spectrum of this reaction mixture is identical with that obtained when the equilibrium is approached from the opposite direction. The eq 1 equilibrium favors the formation of **2**; the K_{eq} value determined by absorption spectroscopy is 1.26 ± 0.06 at 298 ± 0.1 K. The temperature dependence of the equilibrium constant was studied: the parameters $\Delta H° = -3.3 \pm 0.5$ kcal/mol and $\Delta S° = -10.5 \pm 0.8$ cal/(mol·K) were extracted from a plot of ln K_{eq} vs $1/T$.

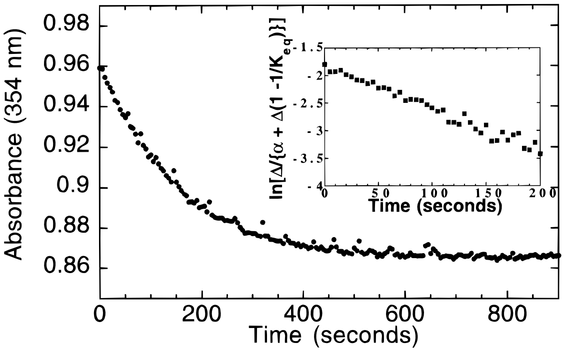

Figure 1. Representative absorption (at 354 nm) vs time plot for nitrogen atom transfer (eq 1) at 298 K. [(salen)Mn≡N]$_0$ = 1.0 × 10^{-4} M and [(5,5′-(MeO)$_2$salchxn)MnCl]$_0$ = 1.0 × 10^{-4} M. The inset shows a plot of ln [$\Delta/(\alpha + \Delta(1 - 1/K_{eq}))$] vs time. k_f was determined using the integrated rate law derived by King.[13]

Kinetics experiments were performed with initial concentrations of the reactants ranging from 0.5 × 10^{-5} to 1.0 × 10^{-4} M.[12] The ratios of the initial starting concentrations were also varied from approximately 1:1 to 1:5. Similar rate constants were obtained regardless of starting concentrations or ratios employed, thus strongly suggesting that the nitrogen atom transfer in eq 1 is first order in each reactant and obeys the integrated rate law for second-order reversible reactions.[13] Plots of ln [$\Delta/(\alpha + \Delta(1 - 1/K_{eq}))$] vs t are linear for more than 3 half-lives. A typical plot is shown in the inset of Figure 1; the rate constant (k_f) for the reaction is 27 ± 6 M^{-1} s^{-1}. From studies of the temperature dependence of the rate, activation parameters $\Delta H^‡ = 10.5 \pm 1.2$ kcal/mol and $\Delta S^‡ = -16.7 \pm 5$ cal/(mol·K) were determined. The relatively small $\Delta H^‡$ indi-

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(8) Salen = *N,N*′-ethylenebis(salicylideneaminato) dianion; 5,5′-(MeO)$_2$salchxn = *N,N*′-(1,2-cyclohexanediyl)ethylenebis(5,5′-dimethoxysalicylideneaminato) dianion.

(9) Cummins and co-workers have observed irreversible nitrogen atom transfer from NMo(OR)$_3$ [R = C(CH$_3$)$_3$] to Mo(NRAr)$_3$ [R = C(CD$_3$)$_2$CH$_3$; Ar = 3,5-C$_6$H$_3$Me$_2$]: Laplaza, C. E.; Johnson, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **1996**, *118*, 709−710.

(10) Formally, N$^-$ is transferred between the two metals to effect the two-electron redox process (Mn^{V}/Mn^{III}). For simplicity, we refer to this process as nitrogen atom transfer.

(11) The nitridomanganese complexes were prepared by modification of a literature method.[7] **2**: ^{1}H NMR (CD$_2$Cl$_2$) δ 8.05−8.01 (d, 2H, N=CH), 7.13−7.07 (m, 2H, ArH), 6.98−6.94 (dd, 2H, ArH), 6.78−6.72 (dd, 2H, ArH), 3.81−3.80 (d, 6H, H$_3$CO), 3.72−3.69 (m, 1H, CH$_2$), 3.54−3.50 (m, 1H, CH$_2$), 3.25−3.19 (m, 1H, CH$_2$), 2.73−2.70 (m, 1H, CH$_2$), 2.59−2.55 (m, 1H, CH$_2$), 2.09−2.05 (m, 4H, CH$_2$), 1.88−1.85 (m, 1H, CH$_2$).

(12) Rates for the nitrogen atom transfer were measured spectrophotometrically by following absorbance changes at 354, 372, 398, and 408 nm using a Hewlett-Packard 8452A diode array spectrophotometer equipped with a thermostated cell holder. T/K (k_f /M^{-1} s^{-1}, K_{eq}): 288 ± 0.1 (16.0 ± 3.0, 1.56 ± 0.25); 293 ± 0.1 (16.3 ± 4.7, 1.31 ± 0.20); 298 ± 0.1 (27.0 ± 6.0, 1.26 ± 0.06); 303 ± 0.1 (41.1 ± 3.6, 1.09 ± 0.11); 308 ± 0.1 (49.2 ± 4.9, 0.98 ± 0.10); 313 ± 0.1 (71.4 ± 7.2, 0.95 ± 0.09).

(13) King, E. L. *Int. J. Chem. Kinet.* **1982**, *14*, 1285−1286. The parameter Δ represents the displacement of a particular concentration at a given time, t, from its equilibrium value, $t = \infty$. A second-order reversible reaction (I) has the integrated rate law (II). $\alpha = [A]_\infty + [B]_\infty + \{([C]_\infty$

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D \qquad (I)$$

$$\ln\left[\frac{\Delta}{\alpha + \Delta\,(1\text{-}1/K_{eq})}\right] = -k_f\alpha t + \text{constant} \qquad (II)$$

$+ [D]_\infty)/K_{eq}\}$ and $\Delta = [A]_\infty - [A]_t = [B]_\infty - [B]_t = [C]_\infty - [C]_t = [D]_\infty - [D]_t$.

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cates that there is bond formation in the transition state that offsets the energy needed to cleave a manganese–nitrogen triple bond.

The activation parameters point to a mechanism involving chloride dissociation followed by nitrogen atom transfer through a nitrogen-bridged binuclear species (eqs 2–4). Since this mechanism predicts that the rate of product formation will exhibit an inverse dependence on the chloride ion concentration (eq 5), studies to determine the influence of added monoanionic axial ligands on the nitrogen atom transfer between **1** and (5,5′-(MeO)$_2$salchxn)MnCl were carried out using tetra-*n*-butylammonium chloride as an external source of chloride. For [Cl$^-$]:[(5,5′-(MeO)$_2$salchxn)MnCl]$_0$ = 1:1, rates at 25 °C decreased by almost 3-fold to $k_f = 10.1 \pm 2.9$ M^{-1} s^{-1}. When this ratio was increased to 2:1, rates at 25 °C fell by an approximate factor of four to $k_f = 7.3 \pm 3.4$ M^{-1} s^{-1}. Since nitrogen/chloride exchange rates between **1** and (5,5′-(MeO)$_2$salchxn)MnCl are inhibited by added Cl$^-$, it appears that Cl$^-$ dissociation is required before formation of the bridged complex.

$$\text{(L)MnCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{(L)Mn}^+ + \text{Cl}^- \tag{2}$$

$$\text{(L)Mn}^+ + \text{(L')Mn}{\equiv}\text{N} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{(L')Mn}^+ + \text{(L)Mn}{\equiv}\text{N} \tag{3}$$

$$\text{(L')Mn}^+ + \text{Cl}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{(L')MnCl} \tag{4}$$

(L)Mn = (5,5′-(MeO)$_2$salchxn)Mn (L')Mn = (salen)Mn

$$k_f = \frac{k_1 k_2}{k_{-1}[\text{Cl}^-] + k_2[(\mathbf{1})]} \tag{5}$$

Rate responses to Mn(III) axial ligand substitutions support the proposed mechanism. Replacement of the axial chloride by iodide increases k_f at 15 °C from 16.0 ± 3 to 25.5 ± 2.8 M^{-1} s^{-1}, while replacing the chloride with acetate decreases k_f at 40 °C by over 2-fold from 71.4 ± 7.2 to 30.9 ± 8.3 M^{-1} s^{-1}. We conclude that the evidence is fully consistent with an N$^-$ transfer pathway involving chloride dissociation (eq 2) followed by the formation and decay of a binuclear μ-nitrido-activated complex, as proposed by Woo for the closely related reaction between (OEP)Mn≡N and (TTP)MnCl.[2,3,14]

We have found that reversible nitrogen atom transfer can occur between two manganese–salen complexes. In doing so, we have demonstrated that this reaction is not unique to metal–porphyrin species. Since the reduction potentials of nitridomanganese Schiff-base complexes can be tuned over a wide range,[15–17] it should be possible to elucidate the influence of electronic interactions on the kinetics and thermodynamics of nitrogen atom transfer reactions.

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(14) H_2OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin; H_2TTP = 5,10,15,20-tetra-*p*-tolylporphyrin.

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