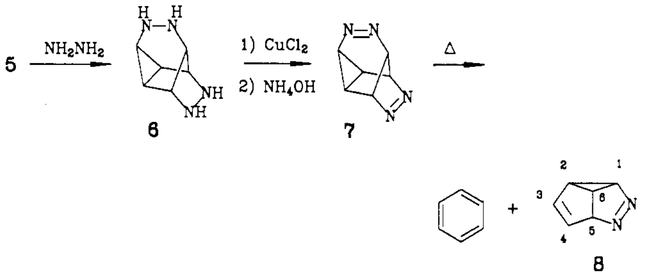
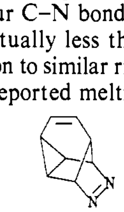
(synthesized from **2**),[26] we propose that the new product has the diazasemibullvalene structure **8**.[27] COSY ^{1}H NMR experiments confirm the connectivity indicated. The small coupling constants between H_2 and H_3, and H_4 and H_5, are consistent with the MM2-predicted dihedral angles of 32° and 41°, respectively.

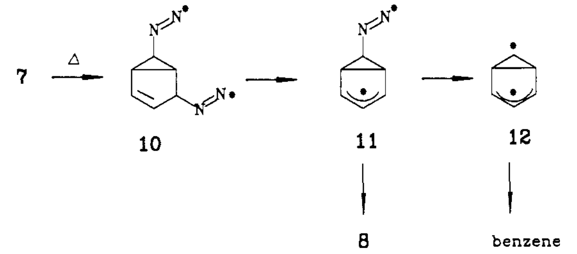


We estimate, on the basis of MM2 and group additivity,[28] that conversion of **7** to benzene + $2N_2$ should be exothermic by ca. 120 kcal/mol. We know of no precedent, however, for a reaction that would cleave all four C–N bonds simultaneously. The bis(azo) compound **7** is actually less thermally stable than would be expected by comparison to similar ring systems.[29] For example, azo compound **9** has a reported melting point of 37 °C and was



9

heated to >50 °C for denitrogenation.[29b] Considerable evidence in the literature[29,30] suggests that 3,4-diazabicyclo[4.1.0]hept-3-enes (such as **9**) thermally decompose by concerted retro-homo Diels–Alder cycloreversions. The lability of **7**, coupled with the formation of **8**, suggests a different mechanism, however. A tentative scheme that would fit our observations is shown herein. Coupled cleavage of both C–N bonds, which are appropriately aligned (NCCN dihedral angle of 167° by MM2), should lower the activation barrier appreciably. The bis(diazenyl) biradical **10** would be expected to rapidly denitrogenate to **11**, which could in turn give **8**. Benzene might arise from formation of "prefulvene[16] biradical" **12** or directly by opening-assisted denitrogenation of **11**.[31]



We are continuing to study the thermal and photochemical reactions of these novel energy-rich azo compounds, and we will report the results of these investigations in due course.

Acknowledgment. Support by the National Science Foundation (CHE-8903155) and the Alfred P. Sloan Foundation is gratefully acknowledged.

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Proton-Coupled Electron Transfer in $[(bpy)_2Mn(O)_2Mn(bpy)_2]^{3+}$

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Oxo-bridged clusters of iron and manganese are important structural and functional units of many redox enzymes, including uteroferrin, hemerythrin, catalase, and photosystem II (PS II).[1] Proposed mechanisms for the binding of O_2 and the catalysis of such reactions as the oxidation of water or peroxide by these enzymes include oxidation or reduction of a metal center and deprotonation or protonation of a bridging oxo ligand. Reversible protonation of oxo clusters in nonaqueous solution has been observed;[2,3] however, coupling of the protonation to a reversible one-electron reduction in aqueous solution has not been shown. While there exists a rich methodology for the electrochemical interconversion of terminal oxo, hydroxo, and aquo complexes of ruthenium and osmium,[4] similar reversible electrochemistry involving bridging oxo and hydroxo ligands has not been demonstrated. We report here that a complex containing the biologically relevant di-μ_2-oxo $Mn^{III}Mn^{IV}$ unit is capable of undergoing net hydrogen atom transfer by proton-coupled electron transfer in aqueous solution.

The mixed-valence dimer $[(bpy)_2Mn(O)_2Mn(bpy)_2](ClO_4)_3$ (bpy = 2,2′-bipyridyl) has been studied extensively as a model for the oxygen-evolving complex of PS II.[3,5-7] The electrochemistry of this complex has been measured in acetonitrile solution[5,6] and shows a reversible one-electron couple at 1.26 V (vs Ag/AgCl), corresponding to the oxidation of the mixed-valence III,IV state to the IV,IV state. There is also an irreversible one-electron cathodic wave, resulting from reduction to the III,III dimer. The pK_a of the oxo ligand of the III,IV dimer is ~2.3 as determined by solution magnetic susceptibility and near-IR spectroscopy.[5]

Our initial attempts to measure the electrochemistry of $[(bpy)_2Mn(O)_2Mn(bpy)_2](ClO_4)_3$ in aqueous solution produced a broad cyclic voltammogram with large (~500 mV) splitting between the oxidative and reductive components. After pretreatment of the glassy carbon working electrode by oxidative activation in 0.1 M H_2SO_4,[8,9] the complex yielded a well-defined, reversible wave with $E_{1/2} = 0.77$ V, $\Delta E_p = 100$ mV at pH 3.78 (Figure 1). This effect has been observed in couples involving terminal oxo, hydroxo, and aquo ligands and has been attributed to electrocatalysis of proton-coupled electron transfer by the activated electrode.[8] The heterogeneous charge-transfer rate[10] obtained from our data is $(5 \pm 1) \times 10^{-3}$ cm/s at pH 3.78, and

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† On sabbatical leave from the Department of Chemistry, Fairfield University, Fairfield, CT 06430.

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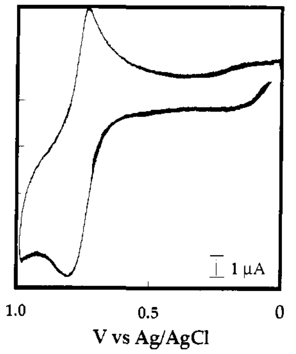

Figure 1. Cyclic voltammogram for 1 mM $[(bpy)_2Mn(O)_2Mn(bpy)_2](ClO_4)_3$ in 0.1 M phosphate buffer, pH 3.78. The potential was held at 0 V for 15 s in order to reduce all of the complex in the double layer before scanning at 50 mV/s. Other conditions were as in footnote 9.

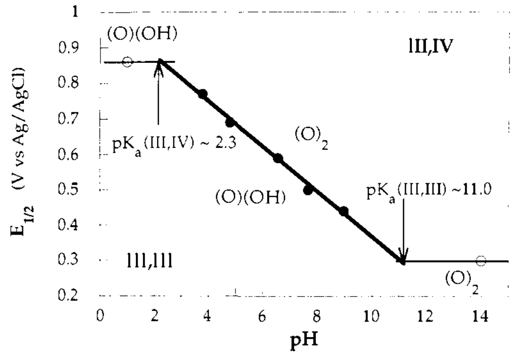

Figure 2. Pourbaix diagram for $[(bpy)_2Mn(O)_2Mn(bpy)_2](ClO_4)_3$. The closed circles are for data taken in 0.1 M phosphate buffer. The peak-to-peak splitting for all of the pH values was between 100 and 130 mV at scan rates less than or equal to 50 mV/s. The heavy line is from a linear least-squares fit to the data (R = 0.997). The open circles represent measurements made in acetonitrile; see text.

we observe good linear correlation (R = 0.998) of peak current with the square root of the scan rate.[11] These observations are also consistent with data obtained from proton-coupled reductions involving terminal oxo ligands.[8]

The pH dependence of the cyclic voltammogram shown in Figure 1 is given in Figure 2 for pH 3–9. The slope is 64 mV/pH unit, which is within experimental error of the 59 mV/pH unit required for a one-electron, one-proton couple.[11] Thus, we assign this wave to the $[(bpy)_2Mn(O)_2Mn(bpy)_2]^{3+}/[(bpy)_2Mn(O)(OH)Mn(bpy)_2]^{3+}$ III,IV/III,III couple, an assignment that is supported by the effects of electrode activation and scan rate described above.

From the measured pK_a of the III,IV dimer,[5] the potential of the pH-independent $[(bpy)_2Mn(O)(OH)Mn(bpy)_2]^{4+/3+}$ couple can be estimated to be 0.8–0.9 V from our pH-dependent data. In fact, addition of a small excess of HPF_6 to an acetonitrile solution of $[(bpy)_2Mn(O)_2Mn(bpy)_2](PF_6)_3$ gives a broad, irreversible wave with E_p = 0.86 V;[12] the same behavior is observed in 0.1 M aqueous trifluoromethanesulfonic acid.[13] Thus, we tentatively assign this wave to the $[(bpy)_2Mn(O)(OH)Mn(bpy)_2]^{4+/3+}$ III,IV/III,III couple. The open circles in Figure 2 represent this value and the known value of the irreversible $[(bpy)_2Mn(O)_2Mn(bpy)_2]^{3+/2+}$ III,IV/III,III reduction.[5,6] As shown, the pK_a of the III,III dimer can be estimated by extrapolation to the pH-dependent region. The estimated pK_a(III,III) of 11.0 is consistent with the known electrochemistry of the III,III species; a high pK_a would be expected for a complex that is unstable in nonaqueous solution but shows reversible proton-coupled behavior in aqueous solution at moderate pH. Thus, the III,III dimer is greatly stabilized by protonation of the oxo group, consistent with the observation of di-μ_2-oxo Mn^{III}_2 complexes only on the cyclic voltammetry time scale.[5,6,14]

There are a number of important biological implications of these results. First, net hydrogen atom transfer to an oxo-bridged cluster can be achieved reversibly. Second, the ability of a redox protein to regulate the effective pH in the active site may play an important role in the energetics of substrate oxidation, especially in reactions with direct proton involvement such as the oxidation of water by PS II or the oxidation of peroxide by catalase. Finally, this observation supports the idea that water oxidation in PS II may occur via binding of water or hydroxide to low-S-state manganese followed by a series of one-electron/one-proton oxidations that yield a high-valent cluster capable of coupling oxo ligands and releasing dioxygen.[1,15]

Acknowledgment. Helpful discussions with Dr. B. P. Sullivan are acknowledged. We thank the National Institutes of Health for support of this research through Grants GM-32715 and GM-40974.

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Separate Pathways for Oxygenate and Hydrocarbon Synthesis in the Fischer–Tropsch Reaction

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Fischer–Tropsch synthesis produces both hydrocarbon and oxygenated products (oxygenates) by reducing CO with hydrogen on a suitable catalyst, among which supported iron, cobalt, and rhodium are examples. Recently we have carried out Fischer–Tropsch reactions on a potassium-promoted supported-iron catalyst using perdeuterated ethylene as an additive to the H_2/CO feed. This was done as a part of a study to investigate the special role that ethylene is claimed to have in the Fischer–Tropsch process, as suggested, in part, by the low concentration of ethylene that is often observed in the products of this reaction.[1] The reaction products were subjected to scrupulous GC–CIMS analysis in order

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