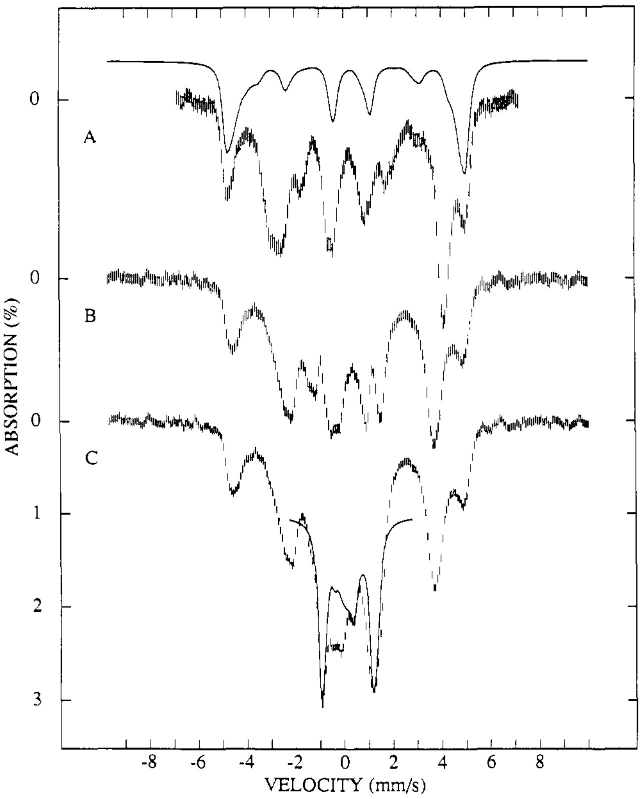

Figure 2. The Mössbauer spectra of *D. gigas* Fd II (A) and $(Ph_4P)[3]$ (C) recorded in a parallel field of 6.0 T at 4.2 K. Spectrum B was obtained by subtracting the theoretical spectrum of low-spin Fe^{2+} subsite 4 (solid line in spectrum C) from the data. The solid line above spectrum A is the contribution of Fe^{3+} subsite 3 in the $[3Fe-4S]^0$ cluster of Fd II.

3) with $A > 0$ and two slightly inequivalent components (subsites 1 and 2) with $A < 0$.[14] Above 100 K, the intensities of doublets 1-3 decrease with concomitant appearance of a new doublet. At 260 K, the spectrum consists of *two* doublets with a 3:1 area ratio, with the new doublet having isomer shift $\delta_{av} = 0.32$ mm/s and quadrupole splitting $\Delta E_Q = 0.70$ mm/s. Correcting for a second-order Doppler shift (0.10 mm/s) and referring δ_{av} to 4.2 K yields $\delta_{av}(4.2\ K) = 0.42$ mm/s. This value corresponds closely to the mean shift of sites 1-3, plausibly suggesting that the new doublet represents a valence-detrapped or valence-delocalized state of these sites.

From the preceding results, we draw these conclusions. (1) The $[Fe_4S_4]^{2+}$ core of **3** contains a unique hexacoordinate Fe(II) subsite which is *low*-spin and thus is not spin-coupled[15] to the remaining $[Fe_3S_4]^0$ cluster fragment (subsites 1-3). (2) The Mössbauer spectra of the fragment convincingly resemble those of protein $[Fe_3S_4]^0$ clusters, and with reference to the spin-coupling correlation diagram for the cluster,[6] the spin of **3** must be $S = 2$. (3) From conclusion 2, the electronic ground state of the fragment consists of a trapped-valence Fe^{3+} ($S = {}^5/_2$) and a delocalized pair ($S = {}^9/_2$). The spectral pattern of Figure 2, parts A and B, has been observed for a variety of core units, viz., protein-bound $[Fe_3S_4]^0$,[9-13] $[Fe_3Se_4]^0$,[16] and $[ZnFe_3S_4]^{2+}$,[15b] as well as for **3**. These observations persuasively suggest that the delocalized pair/Fe^{3+} electronic ground state is intrinsic to a cuboidal $[Fe_3S_4]^0$ cluster and is not a protein-induced property. From the studies reported here and other observations, we anticipate that the synthetic cluster will provide further valuable insights into the static and dynamic properties of the Fe_3S_4 core. The $[Fe_3S_4]^{1+}$ and $[Fe_3S_4]^{1-}$ states are potentially available from chemically reversible redox reactions with $E_{1/2} = -0.18$ and -1.09 V (CH_2Cl_2) vs SCE, respectively. Lastly, the structure at the unique subsite of **3** is likely to be biased toward that at the $Fe(CO)_3$ subsites of $Fe_4S_4(CO)_{12}$.[17] If so, the longer Fe-Fe and Fe-S core distances may facilitate removal of the unique Fe atom to yield cuboidal Fe_3S_4, thus far structurally proven only in supportive protein environments.[8,18,19]

Acknowledgment. This research was supported at Harvard University by NIH Grant GM 28856 and at the University of Minnesota by NSF Grant DMB 86-05050.

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[14] The main difference between the spectra can be attributed to the larger zero-field splitting parameter of **3** ($D \approx -8$ cm^{-1}) vs that of Fd II ($D = -2.5$ cm^{-1}).

[15] In this sense, low-spin Fe(II) has the same function as Zn(II) in the artificial $[ZnFe_3S_4]^{1+,2+}$ clusters of Fd II: (a) Surerus, K. K.; Münck, E.; Moura, I.; Moura, J. J. G.; LeGall, J. *J. Am. Chem. Soc.* **1987**, *109*, 3805. (b) Surerus, K. K. Ph.D. Thesis, University of Minnesota, 1989.

(16) Surerus, K. K.; Kennedy, M. C.; Beinert, H.; Münck, E. *Proc. Natl. Acad. Sci. U.S.A.*, in press.

(17) Nelson, L. L.; Lo, F. Y.-K.; Rae, A. D.; Dahl, L. F. *J. Organomet. Chem.* **1982**, *225*, 309.

(18) Stout, C. D. *J. Mol. Biol.* **1989**, *205*, 545.

(19) Robbins, A. H.; Stout, C. D. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 3639; *Proteins* **1989**, *5*, 289.

Para Photoaddition of *N*-Methyltriazolinedione to Benzene. Synthesis of Energy-Rich Azo Compounds Comprising Benzene + N_2

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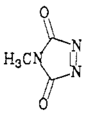
Photoadditions involving benzene have been extensively investigated, yet still attract considerable interest.[2] For simple olefins, 1,3-photoadditions or meta photoadditions to benzene generally dominate, although increasing charge-transfer character often leads to 1,2-additions.[2] On the other hand, 1,4-photoadditions to benzene are most rare and have been suggested in at least some cases to arise from secondary photolysis of ortho adducts[2b] or from stepwise processes.[3] We here report an unusual photochemical [4 + 2] addition to benzene and subsequent reactions of the product. Beyond the novelty of the photochemistry, the resulting adducts open the way to previously unknown energy-rich benzene + N_2 systems.

The wide variety of ground-state triazolinedione (TAD) additions has led to a profusion of interesting azo compounds.[4] To extend the utility of these versatile reagents, we[5,6] and others[7] have been exploring their photoadditions. We have reported that 4-methyl-1,2,4-triazoline-3,5-dione (MTAD, **1**) undergoes photochemical [4 + 2] additions to naphthalene[5] and phenanthrene[6] to give **2** and **3**, respectively. We have now observed a similar addition to the archetypal aromatic molecule, benzene.



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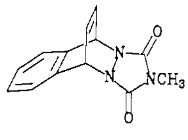

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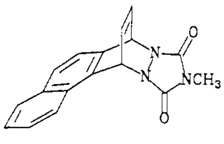

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(1) Fellow of the Alfred P. Sloan Foundation, 1986-1990.

(2) (a) Wender, P. A.; Von Geldern, T. W.; Levine, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 4858 and references therein. (b) Mattay, J. *J. Photochem.* **1987**, *37*, 167 and references therein.

(3) (a) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811 and references therein. (b) Yang, N. C.; Masnovi, J.; Chiang, W.; Wang, T.; Shou, H.; Yang, D. H. *Tetrahedron* **1981**, *37*, 3285.

(4) (a) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762. (b) Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325.

(5) (a) Kjell, D. P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 5368. (b) Kjell, D. P.; Sheridan, R. S. *J. Photochem.* **1985**, *28*, 205.

(6) Hamrock, S. J.; Sheridan, R. S. *Tetrahedron Lett.* **1988**, *29*, 5509.

(7) (a) Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092. (b) Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090. (c) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 3927.

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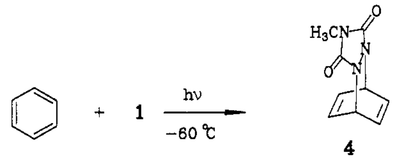
Visible-wavelength irradiation of a <-60 °C solution of benzene and MTAD (ca. 0.1 M each in $CDCl_3$ 2 h in Rayonet photoreactor with Sylvania Cool White fluorescent bulbs) gives a new compound, whose low-temperature NMR spectra (-40 °C, 300 MHz) are consistent with **4**.[8] Appropriately coupled resonances in the olefinic (6.7 ppm) and bridgehead (5.5 ppm) regions appear in the ratio 2:1 in the ^1H NMR. Moreover, the four-line ^{13}C NMR spectrum reflects the C_{2v} symmetry of the adduct. The chemical shifts are quite similar to corresponding resonances in **2**[5] and **3**.[6] On warming of the sample to -10 °C, these signals disappear, with concomitant growth of benzene and MTAD.[9,10]

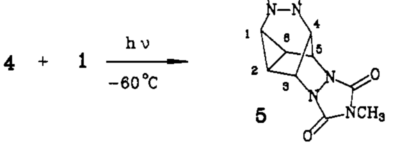


4

We have presented evidence that the photoadditions of MTAD to naphthalene and phenanthrene are concerted.[6] Especially compelling is the observation that the reactions still proceed in glacial acetic acid, which would reasonably be expected to trap a stepwise intermediate; similar intermediates in MTAD thermal additions have in fact been trapped under less favorable conditions.[11] Moreover, the regiochemistry of photoaddition of MTAD to phenanthrene is difficult to rationalize with a stepwise mechanism.[6] In the present case, irradiation of a low-temperature CD_3OD/CD_2Cl_2 (80:20) solution of benzene and MTAD still gives **4**, suggesting (but certainly not requiring) that this addition is also concerted.[12] Finally, although certain photoadditions between aromatics and electron-deficient olefins are thought to involve electron transfer,[13] application of the well-known Rehm-Weller equation[13,14] suggests that electron transfer between benzene and $^1MTAD^*$ would be *endothermic* by >15 kcal/mol and, hence, unlikely.

Para additions to excited-state benzene are rare, whereas ortho additions are somewhat more common, and meta adducts usually predominate.[2] Houk[15] has proposed that this regioselectivity reflects stabilizing interactions between the half-filled molecular orbitals of the electronic configurations making up the B_{2u} (lowest excited singlet) state of benzene and the frontier orbitals of the olefin. In the present case, however, MTAD rather than benzene is electronically excited, and the $n\pi^*$ of this chromophore must be considered. Although photochemical [4s + 2s] reactions are formally forbidden by orbital symmetry,[16] theoreticians have suggested mechanisms whereby very polar photochemical Diels-Alder reactions can become allowed.[17] As we have previously pointed out,[6] the low-energy $^1MTAD\ \pi^*$ interacts most effectively with the same-symmetry HOMO of aromatic systems, leading to three-electron stabilization in the [4 + 2] geometry. Here, the highest singly occupied orbital of $n\pi^*$ MTAD (at -8.0 eV, estimated from the IP[18c] and 0,0 transition energy) energetically better matches the HOMOs of benzene (at -9.25 eV, from IP[18a]) than the LUMOs (at 1.15 eV, from EA[18b]).

In the presence of excess MTAD and with prolonged irradiation times, another compound is formed. Unlike the initial adduct **4**, this product can be isolated and purified by recrystallization from boiling ethanol (>50% yield). The NMR spectra[19] indicate that this product is the bis adduct **5**.[20] The presence of two *N*-methyl groups, the symmetry of the molecule, and the absence of olefinic resonances are evident in both the ^1H and ^{13}C NMR spectra. COSY ^1H NMR analysis also substantiates the skeletal connectivity in the proposed structure.[19] Small vicinal H_2–H_3 (1.1 Hz) and H_3–H_4 (2.2 Hz) couplings are consistent with dihedral angles of 57° and 59°, respectively, predicted by MM2 for **5**. As is often the case in small polycyclic molecules,[21] **5** also exhibits long-range couplings of ca. 1 Hz of H_2 to H_4 and H_5 (similarly for H_6), which complicate the spectra.



5

Conventional basic deprotection/oxidation of the bis adduct **5** resulted in intractable products. Treatment of **5** with *anhydrous* NH_2NH_2,[22] however, produced an air-sensitive product we tentatively identify by ^1H NMR as bis(hydrazine) **6**.[23] Oxidation of a solution containing **6** with aqueous $CuCl_2$ produced a dark-brown precipitate of the corresponding bis(azo) copper complex. Dissolution of this material in cold (-70 °C, 28%) NH_4OH, followed by extraction with $CDCl_3/CCl_4$ (50:50), led to the bis(azo) compound **7**. Low-temperature (-40 °C) ^1H and ^{13}C NMR verified the structure of **7**.[24] The observed chemical shifts of the bridgehead protons adjacent to N rule out either of the two possible monooxidized azohydrazine structures.

The bis(azo) compound **7** is quite thermally labile. Warming the NMR solutions to 0 °C causes rapid disappearance of the signals of **7** ($t_{1/2}$ = 139 s at 0 °C) and the clean formation of an approximately 1.5:1 mixture of benzene and a new product with six distinct protons and carbons. On the basis of the close similarity between the observed NMR and UV spectra[25] and those of the previously well-characterized diazabenzosemibullvalene

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(8) Spectral data for **4**: ^1H NMR (300 MHz, $CDCl_3$, -40 °C) δ 6.69 (dd, J = 4.2, 3.1 Hz, 4 H) 5.48 (tt, J = 4.2, 3.1 Hz, 2 H), 2.91 (s, 3 H) ppm; ^{13}C NMR (75 MHz, same conditions) δ 159.2, 133.3, 53.9, 25.5 ppm. Although the absolute yield of **4** is difficult to obtain due to its thermal instability, quantitative NMR measurements indicate that >80% of MTAD can be converted to **4** under these conditions.

(9) The greater lability of **4** ($t_{1/2}$ = 1 h at 0 °C) compared to **2** and **3** is consistent with the expected gain in aromaticity on cycloreversion. See: Hess, B. A., Jr.; Schaad, L. J.; Herndon, W. W.; Biermann, D.; Schmidt, W. *Tetrahedron* **1981**, *37*, 2983.

(10) For alternate approaches to adducts similar to **2–4**, see: Askani, R.; Schneider, W. *Chem. Ber.* **1983**, *116*, 2355.

(11) (a) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 6376. (b) Smonou, I.; Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1988**, *29*, 2769. (c) Clennan, E. L.; Earlywine, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 7104.

(12) Although both singlet and triplet excited MTAD add to naphthalene,[5] the experiments here only address $^1MTAD^*$. Irradiation of solutions of MTAD where the concentration of benzene is high enough to quench >99% of the fluorescence of MTAD (50:50 benzene/CD_2Cl_2) still gives **4** with no apparent loss of efficiency. The possibility of triplet addition to benzene is under investigation.

(13) Mattay, J. *Tetrahedron* **1985**, *41*, 2393, 2405.

(14) Weller, A. *Z. Phys. Chem. NF* **1982**, *133*, 93.

(15) Houk, K. N. *Pure Appl. Chem.* **1982**, *54*, 1633.

(16) Bryce-Smith and Gilbert have shown that photoadditions of this nature, where the dienophile is excited, are actually formally allowed by MO correlations. Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309.

(17) (a) Epiotis, N. D.; Yates, R. L. *J. Org. Chem.* **1974**, *39*, 3150. (b) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1978**, 135.

(18) (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970. (b) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. (c) Gleiter, R.; Schäfer, W.; Wamhoff, H. *J. Org. Chem.* **1985**, *50*, 4375.

(19) Compound **5**: ^1H NMR (300 MHz, $CDCl_3$, numbered as in text) δ 4.63 (dt, J = 2.2, 1.1 Hz, $H_{3,5}$), 4.47 (tt, J = 2.2, 1.1 Hz, H_4), 3.80 (t, J = 7.0 Hz, H_1), 3.01 (s, 3 H), 2.99 (s, 3 H), 2.08 (d of quart., J = 7.0, 1.1 Hz, $H_{2,6}$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 153.1, 151.1, 58.7, 52.6, 31.8, 26.0, 25.6, 16.1 ppm. Anal. Calcd for $C_{12}H_{12}N_6O_4$: C, 47.37; H, 3.98; N, 27.61. Found: C, 47.46; H, 3.95; N, 26.94.

(20) The second addition of MTAD to **4** is apparently also activated by light; no reaction occurs in the dark under these conditions.

(21) Barfield, M.; Chakrabarty, B. *Chem. Rev.* **1969**, *69*, 757.

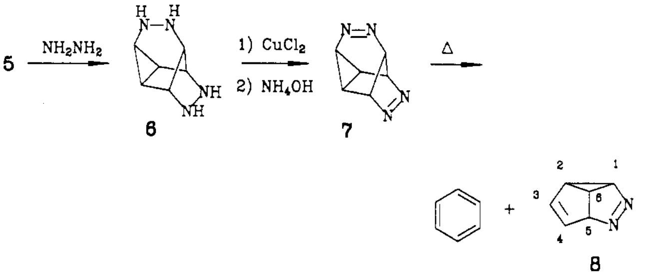
(22) This is a modified procedure of Adam et al.: Adam, W.; Arias, L. A.; DeLucchi, O. *Synthesis* **1981**, 543.

(23) Compound **6**: partial ^1H NMR (300 MHz, CD_3OD) δ 3.53 (m, 2 H), 2.93 (m, 1 H), 2.40 (t, J = 6 Hz, 1 H), 1.58 (d, J = 6 Hz, 2 H) ppm.

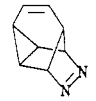
(24) Spectral data for **7**: ^1H NMR (300 MHz, 1:1 $CDCl_3/CCl_4$, -40 °C, numbered as for **5**) δ 5.58 (t, J = 6.2 Hz, H_1), 5.02 (tt, J = 2.2, 1.3 Hz, H_4), 4.62 (dt, J = 2.2, 1.3 Hz, $H_{3,5}$), 2.26 (d of quart., J = 6.2, 1.3 Hz, $H_{2,6}$) ppm; ^{13}C NMR (75 MHz, same conditions) δ 74.24, 74.05, 58.70, 29.24 ppm.

(25) Spectral data for **8**: ^1H NMR (30 MHz, 1:1 $CDCl_3/CCl_4$) δ 5.90 (d of m, J = 5.2 Hz, H_4), 5.60 (ddd, J = 5.9, 5.4, 0.9 Hz, H_1), 5.51 (dd, J = 5.4, 2.0 Hz, H_5), 5.36 (dd, J = 5.2, 2.3 Hz, H_3), 3.28–3.21 (m, $H_{2,6}$) ppm; ^{13}C NMR (75 MHz, same conditions) δ 130.32, 127.58, 91.16, 80.27, 47.35, 44.19 ppm; λ_{max} 342 nm (cf. 340 nm for diazabenzosemibullvalene, ref 26a). Neither the chemical shifts nor the observed coupling pattern is consistent with the hydrazone tautomer of **8**.

(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.

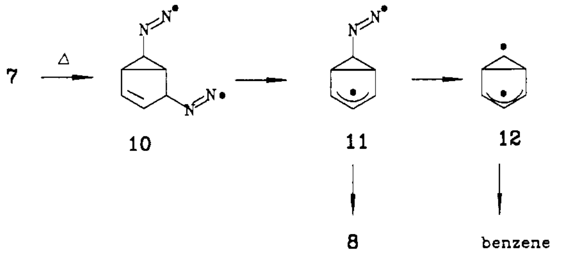


We estimate, on the basis of MM2 and group additivity,[28] that conversion of **7** to benzene + $2N_2$ should be exothermic by ca. 120 kcal/mol. We know of no precedent, however, for a reaction that would cleave all four C–N bonds simultaneously. The bis(azo) compound **7** is actually less thermally 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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(26) (a) Kjell, D. P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 4111. (b) Burger, U.; Mentha, Y.; Thorel, P. J. *Helv. Chim. Acta* **1986**, *69*, 670.

(27) A methylated derivative of the urazole corresponding to this ring system has been isolated: Christl, M.; Kemmer, P.; Mattauch, B. *Chem. Ber.* **1986**, *119*, 960.

(28) Benson, S. W. *Thermochemical Kinetics*, 2nd, ed.; Wiley: New York, 1976.

(29) For comparison with related azo systems, see: (a) Allred, E. L.; Voorhees, K. J. *J. Am. Chem. Soc.* **1971**, *93*, 1300. (b) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680.

(30) Berson, J. A.; Olin, S. S.; Petrillo, E. W., Jr.; Bickart, P. *Tetrahedron* **1974**, *30*, 1639.

(31) It should be noted, however, that no benzvalene, which might be expected from **12**,[26] is observed under our conditions.

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.

(1) (a) Brudvig, G. W.; Crabtree, R. H. *Prog. Inorg. Chem.* **1989**, *37*, 99. (b) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. (c) Vincent, J. B.; Christou, G. *Adv. Inorg. Chem.* **1989**, *33*, 197.

(2) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387.

(3) Hagen, K. S.; Westmoreland, T. D.; Scott, M. J.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1907.

(4) Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C.

(5) Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623.

(6) Morrison, M. M.; Sawyer, D. T. *J. Am. Chem. Soc.* **1977**, *99*, 257.

(7) $[(bpy)_2Mn(O)_2Mn(bpy)_2](ClO_4)_3$ was prepared according to Cooper and Calvin.[5] Satisfactory elemental analysis was obtained, and the reported electrochemistry was reproduced.

(8) Cabiness, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 1845.

(9) Glassy carbon electrodes were prepared according to the procedure of Meyer et al.[8] Activation was run for three cycles of 30 s at 1.8 V and 15 s at −0.2 V. Phosphate buffer (0.1 M) was used from pH 3 to pH 9. Measurements were made with a PAR 273 potentiostat in a cell with a Pt counter electrode and an Ag/AgCl reference. The complex has been reported to be unstable in aqueous solution except in the presence of 0.05 M bipyridyl buffer.[5] We have repeated our measurements in 0.05 M bipyridyl buffer and observe the same $E_{1/2}$ and pH dependence as in 0.1 M phosphate.

(10) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

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